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The Early Development of Stereochemistry and Pasteur's Law. *

BY BAWA KARTAR SINGH, M.A., Sc.D., F.I.C.

The Chemical Society of London, founded in 1841, is the oldest existing society devoted to the furtherance of chemistry. In the earlier years of this society's life, according to Dr. Scott's presidential remarks of 1916, it was thought sufficient for the President to read extracts from the report of the Council, sometimes adding comments on the balance sheet, which hardly filled two pages of the Journal. But with the passage of years, more and more was expected from the President until now, at each anniversary meeting, he is required to deliver a formal address on some subject closely connected with the life of the society as "a body politic and corporate," or on some subject of more purely scientific interest.

The Indian Chemical Society, which came into existence in 1924, was founded with similar aims and objects. Its anniversary meeting is held, in conjunction with the annual gathering of the Indian Science Congress, at different centres of learning with the express purpose of affording an opportunity to its Fellows, scattered all over the country, to take a more active interest in all its affairs. During the first seven years of its existence, both of my predecessors, who have occupied the chair, have set the precedent of delivering presidential addresses on purely scientific subjects.

It is my intention to-day to follow this precedent, and to divide my address into two parts. The first of these will deal with the development of stereochemistry from early times. The second part will deal with what is known as Pasteur's Law, and will contain comments on the results obtained in the chemical laboratory of the Ravenshaw College, Cuttack, on the physical identity of enantiomers—a subject of fundamental importance in the study of optical activity.

Stereochemistry is an experimental branch of the chemical science, and may be regarded as securely founded on the experi-

* Presidential address delivered on the Eighth Annual General Meeting of the Indian Chemical Society, held on the 4th January, 1932 at Bangalore.

mental investigations and theoretical speculations of Pasteur, Kekulé, Le Bel and Van't Hoff. Stereochemical speculations, however, have been prevalent in chemistry since olden times. One of the six schools of Hindu Philosophy—Vaiśeṣika or Atomic Philosophy founded by Kaṇāda†—deals with the atomic theory of matter. The whole universe and the material substances are aggregates of atoms; the atoms are imperishable, the aggregates perish by disintegration. The law of the conservation of matter follows as a necessary corollary from this doctrine. It is thus seen that from very early times in the history of science, matter was believed to be permanent‡, incapable of either annihilation or of creation.

The atomic theory of matter was revived at a much later period by the great classical thinkers of Greece, Leucippus and his successor Democritus (about 460—360 B.C.). Atoms are non-creatable, indestructible and non-changeable. Plato (427—347 B.C.) gave definite geometrical forms to this original matter and thus assigned to it a condition of corporal reality.

Epicurus (341—270 B.C.) assumed all bodies to be modifications of a single homogeneous primary matter. He assigned definite forms to the particles of matter, which was permanent, and of an unchangeable nature. These ideas of the early Greek philosophers were incorporated by the Roman poet Titus Lucritius Carus (96—55 B.C.) in his poetical work, "*De rerum natura*". The problem of the size, weight and form of the atoms was now thrown into the background for lack of experimental data concerning them, and the idea of a *materia prima* captivated the minds of later philosophers. So more than a thousand years passed away without any advance being made

† According to Sir Radha Krishnan, whatever may be the date of Kaṇāda, he is only a systematiser of views which have had a long growth prior to him. He does not believe that his atomic conceptions themselves were later than the time of Leucippus and Democritus (*Indian Philosophy*, Vol. 2, pp. 202-203).

‡ Though the doctrine of the permanence of matter has been accepted from the times of the early Hindu and Greek thinkers, supporters of the opposite idea have never been wanting. In modern times, they are even found among followers of the 'experimental philosophy'. Sir James Jeans is a strong advocate of this opposite idea, and has ably summarised the evidence—astronomical and physical—in support of it (*Nature*, 1931, 128, 108). The annihilation of matter, according to the astronomical evidence, seems to be the only possible source of the energy radiated by the stars, and thus constitutes one of the fundamental processes of the universe. It must, however, be admitted that this hypothesis awaits further observational and experimental data for its final assessment.

in this direction, till we reach the seventeenth century, when the German chemist, Sennert, once more revives the idea that all matter is made up of unchangeable, elementary corpuscles. According to Descartes, (1596—1650), matter is characterised by dimensions, the ultimate particles of matter are the corpuscles, that is the smallest bodies which differ in form and size. Gassendi (1592—1650), a contemporary of Descartes, was also an active supporter of the old atomic theory. According to him, there is a limit to the divisibility of matter, and the ultimate particles of this division are called atoms, which possess size, form and weight. The atoms unite in different ways to form molecules. It appears that the conception of molecules is used here for the first time.

Three chemists were largely responsible for introducing spatial ideas into chemistry as a mental aid. They were Glauber (1604-1670), Boyle (1627-1691), and Lemery (1645-1715). Glauber, a great chemical manipulator and an experimenter, was probably one of the first to point out that crystal form is a characteristic of each salt type, and he recommended its use as a means of chemical identifications.¹

• Boyle pictured his atoms provided with points, hooks and pores owing to the preference given to physiological reactions as a means of recognition of substances in general. The words, "sour", "alkaline" and "salty" are even to-day used as qualitative attributes for chemical substances, being derived from the sensation of taste. Boyle's definition of a salt, "It is easily dissoluble in water, and it affects the palate with a savour whether good or evil", clearly reflects the attitude of mind of the corpuscular chemists, which ascribed to the corpuscles or atoms, the forms of sharp and pointed tools from the analogy of certain mechanical effects which brought forth like sensations.

Boyle in his "Sceptical Chymist", published in 1661, gives further expression to these corpuscular views thus: "Whatever may be the number of elements, one may some day probably be able to demonstrate that they exist as indefinable particles, nevertheless begotten of definite form and size, and that it is the arrangement and combination of these corpuscles which gives rise to the manifold number and varieties of bodies". According to him acids dissolve metals when the pointed particles of the first are congruous with those of the latter. He compares acid particles to knife blades; some of these have only one end encased in a shield; in the case of others

both ends have been put into a shield. The existence of the two chlorides of mercury for instance, is accounted for in this mechanical fashion.

The French chemist, Lemery, propounded his mechanistic corpuscular theory in his book "Cours de Chimie", which first appeared in 1675. This work which had been published in no less than six European languages exerted a profound influence for about a century on the theory of atoms and corpuscles. Chemical character and chemical reactions were determined by spatial factors, *i.e.*, by the form and size of particles. "Acidity of a fluid is due to the presence of pointed particles. An acid is made up of pointed components". The strength of acids was regarded as dependent upon the size and kind of "points" on the particles. The reaction between a given acid and an alkali was thus a question of steric agreement or steric hindrance.

Salt formation through the action of acids upon metals, such as silver nitrate from silver and nitric acid is according to Lemery, an operation in which "the metal is penetrated and reduced to the form of salt by the points of the acid." It is thus seen that the believers in the corpuscular theory of matter regarded the form of corpuscles as the deciding factor in differentiating different kinds of salts, acids, and bases.

The great development in mechanics in the seventeenth century associated with the names of Galileo, Kepler and Newton exerted a powerful influence, and chemists of that period were not slow in giving mechanical explanations of chemical phenomena. The mechanical ideas, however, did not prove quite satisfactory in explaining chemical phenomena. When an acid acts on a metal, the particles of both come into immediate contact. So far the process can be regarded as mechanical, but further mechanical explanation is lacking as to what takes place *after* the reacting particles of the acid and metal collide with one another.

It should be mentioned that protest against these mechanistic explanations, with the aid of points, thorns, pores, screws, clasps, etc., of the particles was not wanting even at that time. It was made by John Kunckel, the great physician, in his book, "Laboratorium Chymicum" (p. 133) published in 1722.

It is, however, interesting to note that mechanics once more, in these days, is coming into closer relationship with chemistry. These newer ideas are based not on the classical mechanics of the seven-

teenth century, but on the modern theory of wave-mechanics or quantum-mechanics associated with the names of Broglie, Heisenberg and Schrödinger.

We have seen that the speculations of the seventeenth century had attempted to solve the question of the form of particles by means of a mechanistic hypothesis. The eighteenth century supplied a new scientific weapon, namely crystallography, in obtaining definite evidence concerning form itself. Two French crystallographers stand out as great pioneers in this development, *e.g.*, Romé de l'Isle and René J. Haüy. The latter correlated crystalline form and chemical composition. This early crystallographic work proved of great value in the succeeding century in the formulation of ideas regarding the spatial arrangement of atoms in the molecule.

In 1808 Dalton published his "New System of Chemical Philosophy" and propounded fundamental concepts of great importance, namely, the atomic theory and the laws of chemical combination. In the same year Wollaston² introduced spatial ideas about atoms. He says "We shall find that the arithmetical relation alone will not be sufficient to explain their mutual action, and we shall be obliged to acquire a geometrical conception of their relative arrangement in all three dimensions of solid extension". The molecular theory developed by Ampère and Avogadro in conjunction with crystallography, was instrumental in extending these ideas of spatial arrangement of atoms. The association of the idea of a spatial environment with the structure of an organic molecule began to be more commonly accepted as a mental picture as is seen in Laurent's kernel theory (1837). It was based on Haüy's theory of crystal structure. Leopold Gmelin³ deserves much credit for giving us for the first time, a clear account of stereochemical conceptions. He directed attention to the idea of relative position of atoms in the molecule, as this may lead us to arrive at a proper conception of the constitution of organic compounds.

The discovery of the Law of Isomorphism by E. Mitscherlich⁴ in 1819 "Crystal form is independent of the chemical nature of atoms and is determined only by the number and relative position of the atoms" was of very great assistance in fixing the relative atomic weights of elements, and thus gave great stimulus to the development of the Atomic Theory. The discovery of the phenomenon of isomerism by Gay-Lussac⁵ soon after—according to which substances may exist which have the same composition, but which may

be different physically and chemically—proved to be of immense value in the evolution of the theory of molecular structure of organic compounds. The synthesis of urea from ammonium cyanate by Wöhler in 1828—the first classical example of an organic product built up in the laboratory—broke down the distinction of a 'vital force' in the chemistry of living and non-living matter. This is also one of the earliest examples of a pair of isomeric substances. Rapid strides which were now made in organic synthesis led to a remarkable increase in the number of isomeric compounds. The older theories of structure were found to be inadequate to accommodate all this new knowledge of isomeric phenomena, and led Kekulé in 1858 to propound his theory of molecular structure, based on the hypothesis of valency and the law of linking of atoms. As is often the case in the history of this subject, this great development was brought about by Kekulé when he was only 29 years old. The circumstances under which he got the inspiration are recorded by him in a speech^{5a} before the German Chemical Society. "One fine summer evening I was returning by the last omnibus, 'outside' as usual, through the deserted streets of the metropolis (London), which are at other times so full of life. I fell into a reverie (*Traümerie*), and lo, the atoms were gambolling before my eyes. Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time, I had never been able to discern the nature of their motion. Now, however, I saw how, frequently two smaller atoms united to form a pair; how a larger one even embraced two smaller ones; how still larger ones kept held of three or even four of the smaller; whilst the whole kept whirling in a giddy dance". As a result of the great advance made by Kekulé, the conception of molecular constitution followed as a necessary corollary of this new doctrine, and led to clearer ideas about the constitution of chemical compounds by means of their graphic formulae. The theoretical scheme of Kekulé proved, however, insufficient to embrace all the known facts, until in 1874, Van't Hoff and Le Bel, independently demonstrated the all important part which molecular configuration plays in the interpretation of certain cases of isomerism in organic chemistry. The evolution of the theory of molecular structure into that of molecular configuration was brought about by the discovery of two pairs of acids, which were destined to play an important part in the development of stereochemical ideas, namely, racemic acid (Gay-Lussac, 1826) isomeric with tartaric acid, and lactic acid (Scheele,

1780) isomeric with paralactic acid or sarcolactic acid. This advance is due to the crystallographic investigations of Pasteur (1848-1860) on the first pair of acids and their salts. Previous to this in 1841 de La Provostaye had carefully determined the crystal forms of tartaric and racemic acids and their salts. Mitscherlich in 1844 published the results of his crystallographic examination of the sodium-ammonium salts of racemic and tartaric acids, stating that these double salts "have the same chemical composition, same crystalline form and angles, identical specific weights and double refraction, in consequence of which their axes form the same angles. Their aqueous solutions have the same refraction. However, the dissolved tartrate rotates the plane of polarised light, whereas the other is indifferent, a fact which had previously been noted for this whole series of salts by Biot". "But", continues Mitscherlich, "*the nature and the number of atoms, their arrangement and their distance from one another are the same in both bodies*"⁶. This conclusion, at the time of its publication, especially concerned Pasteur who was then only 22 years old, and was still studying at the Ecole Normale, and four years later acted as a stimulus for a whole series of new experimental and theoretical investigations. But the course of development of Pasteur's ideas, culminating in his theory of Molecular Dissymmetry, is logical and is yet another instance which illustrates that the progress of chemistry has been mainly achieved as the result of the coordination of observed facts with a series of hypotheses, each closely related in point of time to the one preceding it. It also shows the truth of the remarks of Laplace, "The essence of a discovery lies in the combination of ideas that are fit for combination, and that were hitherto isolated." An account of this development of ideas has been left to us by Pasteur in his two famous lectures⁷, "Concerning the asymmetry of naturally occurring organic compounds," delivered before the Chemical Society of Paris in 1860. His theory of molecular asymmetry is the foundation on which modern stereochemistry rests. At the time of his researches, the theory of molecular structure of Kekulé* had not come into existence. It was,

* The lack of this knowledge is reflected in an error, which Pasteur made in connection with his researches on malic acid. He erroneously concluded that every asymmetric substance must exist in four different forms (Lectures on molecular dissymmetry, 1860). The number of isomeric forms into which an asymmetric molecule may exist, cannot always be predicted without a knowledge of its structural formula, which was, however, unknown at that time. Even this error led him to discover the fourth tartaric acid, namely, the meso, the internally compensated variety.

therefore, not possible to depict structurally the organic compounds by the graphical representation of atomic linkage, and even the two dimensional formulæ, limited as they are as a true picture of the molecule, were unknown at that time. His studies on the influence of molecular asymmetry of natural organic products on living matter is the direct outcome of his early crystallographic work, and is a most surprising chapter of stereochemistry," "which," he says, "opens up a new, distant, but definite horizon for physiology."

We should now revert to consider this early development of ideas in the mind of Pasteur and follow closely his line of thought. Haüy and Weiss recognised the occurrence of hemihedral faces upon quartz and that these faces in certain individuals lay to the right and in others to the left. Biot (1813) had found that quartz crystals could be divided into two groups as regards their behaviour towards polarised light; one turned the plane of polarised light to the right, the other to the left, but to an equal extent. Two years later he discovered that organic liquids (oil of turpentine) and aqueous solutions of tartaric acid and sugar also possess optical activity. Biot further showed in 1817 that matter in the gaseous state also exhibited this property, as in the case of the vapour of turpentine. The property of optical activity is thus exhibited by matter in all the three states of aggregation, solid, liquid and gaseous. Herschell subsequently (1820) correlated these hitherto isolated facts by suggesting a connection between the crystal form and optical rotation; and the thought was fully confirmed by experiment in that those quartz crystals with right hemihedral faces turned the plane of polarised light to the right and those with left hemihedral faces turned the plane of polarised light to the left. Thus a fruitful relation between hemihedrism and optical rotation of crystalline substances (such as quartz, *etc.*) was discovered. Pasteur, at the outset of his brilliant scientific career repeated the previously mentioned investigation of de La Provostaye on the crystal form of tartaric acid, racemic acid and their salts. He discovered something which had been overlooked by the great physicist, namely that all crystals of the tartrate possessed hemihedral faces, and correlated this hemihedrism of the tartrates with the previous observations of Biot on their optical activity. He thus established the same kind of parallelism between hemihedrism and optical rotation for tartaric acid and tartrates, both in the crystalline state and in solution, as had previously been found by Herschell for quartz. Pasteur further investigated the crystal form of racemic

acid which showed no hemihedrim, and it had been shown by Biot that aqueous solution of this acid was inactive towards polarised light. In this way his first idea of a possible connection between the hemihedrim of the tartrates and their optical activity was converted into one of certainty, so far as Pasteur was concerned. But how were these facts to be brought into harmony with the previously mentioned observations of Mitscherlich, who had found in 1844 that the crystal forms of the sodium-ammonium salts of racemic and tartaric acids were completely identical? Pasteur, at once concluded that Mitscherlich had erred in one point. Apparently he had failed to observe that the double salt of tartaric acid is hemihedral, while that of racemic acid is not. In order to clear up this point, Pasteur repeated this work on the crystalline form of both of Mitscherlich's salts with the utmost care. He observed that the double salt of racemic acid crystallised with hemihedral faces, some of which were oriented to the right, others to the left. The two types of crystals were separated from one another, and their aqueous solutions of equal concentration were examined in the polarimeter. He then found with no less surprise than pleasure, that the solution of the salt with right hemihedral faces was *dextro*-rotatory, and that of the salt with left hemihedral character was *laevo*-rotatory to an equal extent, further, on mixing these two solutions, optical activity disappeared. The emotions which must have stirred the mind of the young investigator were so great that he was unable to remain at the polarimeter. These experiments were later repeated by Pasteur in the presence of Biot, and an account of the dramatic scene which ensued had been left on record by Pasteur himself⁷. The illustrious old physicist was visibly moved so much that he seized Pasteur's hand and exclaimed: "My dear child, I have all my life so loved this science that I can hear my heart beat for joy". The correct explanation of these facts was given by Pasteur: on crystallising the optically inactive sodium-ammonium racemate, the salt must have separated into its *dextro*- and *laevo*-rotatory components. The *dextro*- and *laevo*-tartaric acids were obtained from the optically active salts in a pure state, and possessed equal and opposite rotation. When a mixture of equal weights of the two acids was crystallised, the product was identical with racemic acid. Pasteur's acute judgment at once led him to conclude that the molecules of the two tartaric acids were the same in composition and structure, differing in spatial arrangement such that one was the enantiomorph of the other. This

would be the case only, if their configurations were tridimensional, and were related to one another as an object is to its non-superposable mirror image, owing to the existence of "molecular dissymmetry". This view is altogether correct; it is of more universal application than the later view of Le Bel and Van't Hoff. Whenever the molecular configuration is such that it is different from its mirror image there is a possible isomerism in which the two isomers are related to one another as the right hand is to the left. In the solid state they show enantiomorphic crystals, and in solution opposite optical activity.

The above mentioned work on sodium-ammonium racemate enabled Pasteur to discover the first of his classical methods for the resolution of racemic substances into their optical antipodes. The second, salt formation by means of optically active bases, and subsequent fractional crystallisation, followed in 1853. The third method⁸, involving the destruction of one of the active forms by means of micro-organisms, was discovered in 1858.

As it is already pointed out, the theory of Kekulé had not yet been propounded, and therefore, it was not possible for Pasteur to point out more precisely the spatial arrangement of the atoms in the molecules. The insufficiency of two-dimensional formulae of Kekulé was gradually being recognised, and other suggestions of three-dimensional models of molecules were now forthcoming. Butlerow deserves special mention in this connection. He thus wrote in 1862, 'Let us take a simple example, and assuming that all four valency units of tetravalent carbon are different, let us give it the form of a tetrahedron, where each of the four surfaces may combine with one equivalent of hydrogen.'⁹ In 1863 he was even more decisive with the idea of spatial arrangement, when he said¹⁰, "If atoms really exist, I cannot see why all attempts at determining their spatial arrangement are useless, as Kolbe would have us believe. Why should not the future teach us how to make such determinations?" Even Kekulé, the inventor of two-dimensional formulae was not unaware of spatial models, when he said, "The incompleteness of the older models may be avoided, if the four valencies of carbon instead of being represented in a plane, are directed along the axes of a hexahedron starting from the atomic sphere itself and ending in the planes of a tetrahedron."¹¹ In 1869 several chemists put forward spatial ideas. Ladenburg's prism formula for benzene¹² and its representation by six tetrahedrons by Rosenthiel clearly involved spatial considerations. Wislicenus' work on the three modifi-

cations of lactic acid, which could not be explained on the two-dimensional formulae of Kekulé, forced him to write thus in this connection: "The facts compel us to explain the difference between isomeric molecules possessing the same structural formula by the different arrangement of their atoms in space."¹³

These ideas of spatial arrangement of the atoms in a molecule had taken definite hold of the mind of Van't Hoff, who was then only 22 years old. He gave them a mathematical form in his small pamphlet^{13a}, published in Dutch in September, 1874. A mere detailed account of this work appeared in the following year, in the French language, under the title: "*La chimie dans l'espace.*" The circumstances, under which the discovery of the idea of the asymmetric carbon atom were made, are thus given by Van't Hoff in 1904: "At that time (1873) I had been studying Wislicenus' paper on the lactic acids at the University of Utrecht, and when about half way through the article, I decided to stop my work, and take a walk. It was during this walk, under the influence of fresh air, that the idea of an asymmetric carbon atom occurred to me."

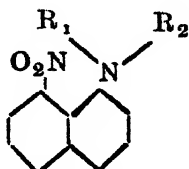
At about the same time (November, 1874) Le Bel¹⁴ published independently similar views on molecular symmetry and optical rotation. The conceptions of the two young investigators were not quite the same. Van't Hoff based his theory on Kekulé's law of the quadrivalency of carbon with the added hypothesis of the tetrahedral environment of the four valencies of the carbon atom. Le Bel's starting point was the researches of Pasteur.

The Le Bel-Van't Hoff theory of the asymmetric carbon atom may be briefly stated thus: If a molecule contains a carbon atom linked to four different substituents, the spatial distribution around the atom becomes asymmetrical, and this may be effected in two different ways, the one being the non-superposable mirror image of the other. The conception of the asymmetric carbon atom involves the idea of the "chemical contrast" between the substituents as well as their dissymmetric spatial arrangement.

The doctrine of the asymmetric atom has done great service in the development of stereochemistry^{14a}. It is a useful guide in deciding whether an optically inactive substance can be resolved into its optically active components. In this way, elements other than carbon were shown to furnish optically active substances in which the enantiomorphism is associated with the presence of an asymmetric

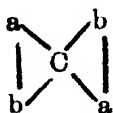
sulphur ¹⁵, selenium ¹⁶, tin ¹⁷, silicon ¹⁸, boron ¹⁹, nitrogen ²⁰, or phosphorus atom ²¹.

We may now cite cases to illustrate the inadequacy of the theory of the asymmetric atom by showing that the presence of such an atom in a molecule is not always a necessary condition for the occurrence of enantiomorphously related isomers. These cases include the complex metal compounds of Werner ²², Berylliobenzoylpyruvic acid of Mills ²³, potassium disalicylborate of Boësen ²⁴, 1-methylcyclohexylidine-4-acetic acid of Pope, Perkin and Wallach ²⁵, 6:6'-dinitrodiphenic acid and other compounds of the diphenyl series of Kenner ²⁶, and a derivative of 8-nitro-1-naphthylamine of Mills ²⁷:

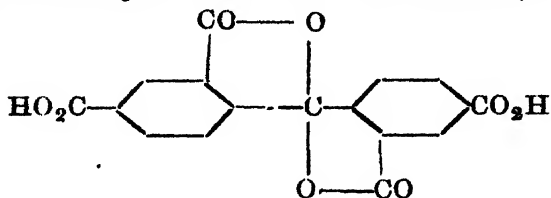


(in which $R_1 = C_6H_5SO_3$ and $R_2 = -CH_2 \cdot COOH$).

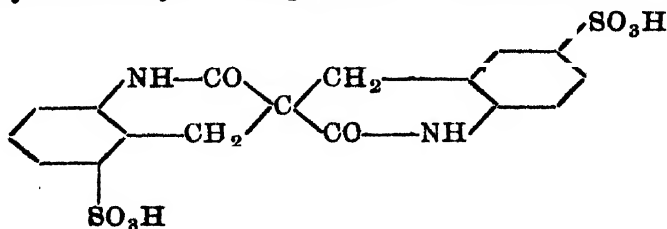
Another class of molecularly dissymmetric substances is formed by spirocyclic carbon compounds of the type



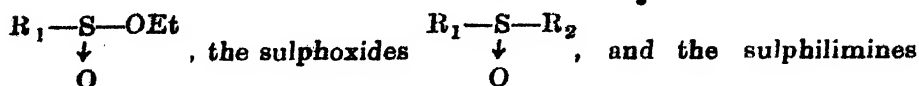
The first substance of this kind to be investigated was the ketodilactone of benzophenone-2:4:2':4'-tetracarboxylic acid ²⁸,



and this was followed by another representative of this class, namely, bisdihydrocarbostyryl-3:3'-spirane-6:6'-disulphonic acid ^{28a}.



A number of compounds of 3 co-valent sulphur obtained by Phillips²⁹, which belong to the sulphonic esters,



$\begin{array}{c} R_1-S-R_2 \\ \downarrow \\ N \cdot SO_2R \end{array}$ are of very great interest, as the molecular dissymmetry of this group of compounds is brought about by only three radicles attached to the central atom.

In all cases, these compounds have been separated into their optically active antimers. It is thus evident that the Le Bel-Van't Hoff idea is only a very special case covered by Pasteur's more universal principle. It applies only to the case, not even a simple one, in which on account of the wholly asymmetric spatial distribution around one of the atoms, the molecule lacks all symmetry. The conception of Pasteur, however, covers all cases; those in which it is possible to single out an asymmetric atom, and others where molecule does not contain such an asymmetric atom, but possesses enantiomorphous molecular configuration brought about by a dissymmetric distribution in space even by identical substituents. The "chemical contrast" between the substituents involved in the Le Bel-Van't Hoff hypothesis is not absolutely necessary. It is possible for the molecule as a whole to show a non-superposable symmetry of its configuration, even if the substituents of the complex are identical. The remarkable series of optically active co-ordination compounds of the metals of which triethylenediamine cobaltic chloride $[Co'''(en)_3]Cl_3$ and potassium chrome oxalate $[Cr'''(C_2O_4)_3]K_3$ of Werner²³ are examples, form a class of substances in which the molecular dissymmetry is associated with very great degree of symmetry of chemical constitution brought about by identical substituents.

Pasteur's Law: The Absolute Identity of the Physical and Chemical Properties of Enantiomers.

As already mentioned, Pasteur through his brilliant researches on racemic and tartaric acids discovered the special isomeric relations of the molecules of the same structural formula which are related to each other as an object is to its non-superposable mirror image. Though the great French Savant was not able

to indicate the precise spatial arrangement of the atom in the molecule, he, at once, realised that his epoch making discovery made it absolutely necessary to recognise the fact that any wholly successful representation of the organic molecule must be extended in tri-dimensional space. He significantly asks, "Are the atoms of the *dextro* acid arranged in the form of a right-handed spiral, or are they situated at the corners of an irregular tetrahedron, or do they have some other asymmetric grouping? This we do not know. But without doubt the atoms possess an asymmetric arrangement like that of an object and its reflected image" ⁷.

The Identity of Chemical Properties.—In this way, Pasteur was able to classify organic compounds into two great groups; symmetrical compounds with enantiomorphous reflected images. He showed that the identity of chemical properties in the case of enantiomorphous compounds, like the two tartaric acids and their derivatives, persists so long as they are brought together with bodies of the first category, *e.g.*, potassium hydroxide, sodium hydroxide, ammonia, alcohols and ethers; in short with all bodies without asymmetry. With such bodies which are devoid of asymmetry, the enantiomorphous forms do not affect the action of chemical affinity.*

On the other hand, if they are subjected to the action of bodies of the second class, which are themselves asymmetric, then the two products which are formed no longer identical in their properties. They differ in solubility, crystalline form, specific gravity, and the amount of water of crystallisation, since they are no longer enantiomorphous, and may differ from one another quite as much as the most distantly related isomers. It is thus seen that molecular asymmetry may alter the action of chemical affinity. It will be seen that Pasteur discovered his second method (salt formation) of resolution of racemic compounds into their optically active components as the result of his theoretical speculations and the above mentioned close reasoning into the nature of molecular dissymmetry. It was not due to any chance occurrence, as is the case with his first (spontaneous crystallisation) and third (biochemical) method.

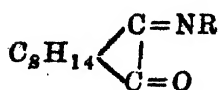
The Physical Identity of Enantiomers.—According to Pasteur's principle of molecular dissymmetry, enantiomorphous molecular

* The velocity constant of mutarotation of the *d*- and *l*-oxymethylenecamphor in benzene solution is practically identical (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1930, 7, 771). This shows that the enantiomers are identical as regards the rate of chemical change involved in the process of mutarotation.

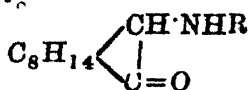
configurations must possess the same total energy. They must show similar mechanical stability, and, therefore, have an equal chance of being produced. They must also possess the same scalar properties, such as density, crystal lustre, solubility, refraction, dispersion. But they must differ in these physical properties, which are of the directional (vectorial) nature, such as, for example, direction of rotation of the plane of polarisation of polarised light, unsymmetrical distribution of the hemihedral facets in their crystal forms, and also in the enantiomorphous distribution of pyro- and piezo-electrical polarity. The magnitude of these vectorial properties is, however, identical for the enantiomorphous forms. These results follow from classical mechanics. On the other hand, according to wave-mechanics ³⁰, the *dextro*- and *laevo*-forms of a compound differ in energy and in rotatory power, although perhaps only to a very slight extent. The two views thus lead to different results. In support of the view derived from wave-mechanics, slight but distinct differences are alleged to exist in the rotatory power and other physical properties of the *dextro*- and *laevo*-forms of mandelic and camphoric acids ³¹. But Pasteur's Law of Molecular Dissymmetry is too fundamental to be dismissed by a few isolated observations; the discrepancies in these cases may very well be due to some impurities in the substances examined. It seems impossible that the *d*- and *l*-forms of a compound could be other than an object and its non-superposable exact mirror-image, agreeing precisely in every detail of structure and of properties, except those of a vectorial nature, which differ in sign, but otherwise identical in the numerical magnitude in all cases. Moreover it must be borne in mind that the wave-mechanics of rotatory polarisation is, at present, in a rather unsatisfactory condition.

With the object of testing the validity of Pasteur's Law as regards the equality in the numerical value of the rotatory power of the opposite active forms, an extended series of investigations on the rotatory dispersion of enantiomorphous forms was undertaken in 1926. The first paper on this subject was published in 1930, and since then seven communications ³² have appeared in our Journal and in the Transactions of the Faraday Society. An equal number of papers dealing with this subject, and other aspects of the problem still awaits publication. The compounds, which have been examined, belong to the aryl derivatives of iminocamphor, amino-

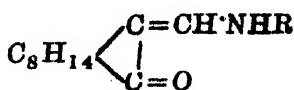
camphor, aminomethylenecamphor, and the corresponding bis derivatives of the following types (I-VI):



(I)

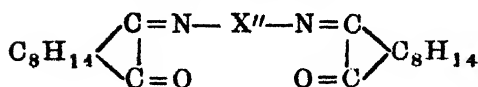


(II)

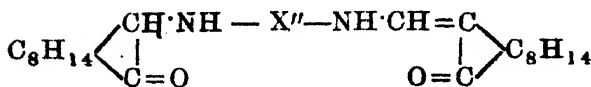


(III)

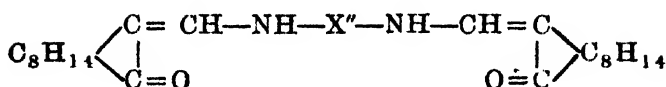
(R = a monovalent radicle).



(IV)



(V)



(VI)

(X'' = a divalent radicle).

The rotatory powers of the *d*- and *l*-forms have been examined in six solvents for about eight wave-lengths in the visible region of the spectrum (λ 6708 to 4358 Å.U.) at 35° and at almost identical concentrations. Out of about 1600 observations on the rotatory power which have been recorded³² and those which still await publication, the differences in the specific rotatory power of the *dextro* and *laevo* forms correspond to a difference which is within 0.01° in the observed angle of rotation in 80 per cent. cases, between 0.01° and 0.02° in 17 per cent. cases, between 0.02° and 0.03° in 2.5 per cent. cases, and between 0.03° and 0.04° in the remaining one half per cent. cases, the maximum deviation allowable in such observations being 0.02° in the observed angle of rotation. The three per cent. cases, in which the differences are slightly greater than the maximum allowable deviation (0.02°) for certain wave-length, give values for rotatory power for other wave-lengths, which are within this

• maximum error. This shows that these deviations are of the nature of casual experimental errors. By way of illustration, the rotatory dispersion of the *d*- and *l*-forms of aminomethylenecamphor³³ is given in Table I.

TABLE I.

Aminomethylenecamphor.

$t=35^{\circ}$; $l=2$ dcm.; solvent = pyridine.

Concentration (g. in 100 c.c.) of *d*-form = 3.0016.

,, ,, ,, l-form = 3.0024.

Line.	<i>d</i> -form.		difference in [α] of <i>d</i> - and <i>l</i> -forms.	<i>l</i> -form	
	α	[α]		α	[α]
Cd ₅₀₈₆	+28°31'	471·7°	-0·3°	-28°34'	472·0°
Ag ₅₂₀₉	26°35	438·9	+0·1	26°35	433·8
Hg ₅₄₆₁	22°96	382·	-0·14	22°97	382·5
Hg ₅₇₈₀	19°58	326·15	-0·05	19°59	326·2
Na ₅₈₉₃	18°61	309·9	+0·4	18°60	309·5
Li ₆₁₀₄	16°93	282·1	-0·1	16°94	282·2
Cd ₆₄₃₈	14°74	245·5	-0·1	14°75	245·6
Li ₆₇₀₈	13°32	221·9	+0·05	13°32	221·85

The recent observations of Darmois³⁴ on the rotatory power of the *d*- and *l*-forms of the complex ammonium salts of molybdic and malic acids of the formula $[4 \text{ MoO}_3, 2 \text{ C}_4\text{H}_4\text{O}_5] (\text{NH}_4)_4 + 5 \text{ H}_2\text{O}$, for mercury green light, show that the observed angles of rotation do not differ by more than 1 part in 1000 parts. This is also the accuracy attained with aminomethylenecamphors (Table I).

These results clearly support Pasteur's principle of molecular dissymmetry, according to which the *d*- and *l*-forms are represented as true mirror images of one another, differing in sign, but absolutely identical in the numerical value of the rotatory power.

In conclusion, I wish to make an observation, which may serve to inspire and encourage younger chemists. It is this: on no account are they to be deterred from making bold speculations and experiments in fields which have already been trodden by more

experienced and older workers. It often happens that the latter have lost that plasticity of mind, which alone can produce or receive fruitful ideas. The account of the evolution of the theories of molecular configuration of organic compounds, which I have attempted to-day, shows that this subject has been exclusively developed, so far as fundamental concepts are concerned, by young men, at the very threshold of their career—Pasteur, Kekulé, Van't Hoff and Le Bel.

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On a Test of the Rival Theories of Active Nitrogen.

BY B. D. CHHADRA AND H. R. LUTHRA.

The excitation of the so-called forbidden lines has of late aroused considerable interest. Success in such experiments has however been rare with atoms of low atomic weight. The experiments described in the following pages were undertaken to obtain the forbidden lines of sulphur. The arguments which justified the procedure adopted in this investigation may be briefly described as follows: When a condensed electric discharge is passed through nitrogen streaming in a tube, the gases which come out continue to glow with a golden yellow colour (Lewis, *Astrophys. J.*, 1904, 20, 49). The exact nature of this after-glow (also called 'active nitrogen') is not even now fully understood.

• Birge (*Nature*, 1924, 124, 642) assumes the existence of a metastable molecule with an energy content of about 14 volts. On collision (of the second kind) with an atom of another element it gives up its energy and the latter in turn becomes luminescent giving out its characteristic lines (Klein and Rosseland, *Zeitsch. Physik*, 1921, 4, 46).

Sponer (*Z. Physik.*, 1925, 34, 622) studied the spectrum of nitrogen and active nitrogen, and basing her arguments on the analysis of the band spectrum of nitrogen, previously carried out by Birge (*National Research Council Bulletin*, No. 57, 244) showed that the spectrum of active nitrogen consists of a few selected bands of nitrogen and that the strongest bands of active nitrogen correspond to vibrational quantum number $n=11$, of an electronic state of N_2 which he calls 'B'. Assuming that the non-polar nitrogen molecule breaks up into its constituent unexcited atoms under the action of a condensed discharge, and gives rise to the phenomenon of active nitrogen, we get from this hypothesis the dissociation potential of nitrogen as 11.4 volts. The long life of active nitrogen is inconsistent with the idea that the chances of the two atoms directly combining to form a molecule are very remote, for in this case the laws of conservation of energy and momentum would not be satisfied.

Some fresh light on the subject has recently been thrown by the investigations of Compton and Boyce (*Physical Rev.*, 1929, ii, 33, 145) on the analysis of the arc spectrum of nitrogen in the Schumann region and the excitation of the auroral green line λ 5377 by Kaplan (*Nature*, 1928, 121, 711) by a rather interesting method. Kaplan (*loc. cit.*) photographed the spectrum of active nitrogen formed from a mixture of 96 p. c. nitrogen and 4 p. c. oxygen and observed the auroral line. He explained its presence by postulating the presence of metastable atoms of nitrogen loaded to an energy of 2.87 and 3.56 volts. The presence of these metastable levels in the spectrum of nitrogen was indicated by the work of Compton and Boyce (*loc. cit.*) and Kaplan suggested that since the auroral green line was a forbidden line of oxygen atom and required about 3 volts for its excitation, it could be developed only under very special conditions. The nitrogen atoms in the after-glow which are loaded with a restricted amount of energy are very favourable for its production. This hypothesis by Kaplan (*loc. cit.*) is extremely interesting but evidently needs further experimental support:

The most stable configuration of the oxygen-like atoms gives rise to $^3P_{0, 1, 2}$, 1D_2 and 1S_0 terms. The 3P terms were obtained by Hopfield (*Physical Rev.*, 1927, ii, 29, 924) and the singlet terms for oxygen have recently been identified by Frerichs (*Physical Rev.*, 1929, ii, 34, 1239) and he has conclusively shown that the auroral green line corresponds to $^1D \rightarrow ^1S$ transition.

In the course of an investigation of the spectra of selenium and tellurium, McLennan and Crawford (*Nature*, 1929, 124, 874) were able to identify the $^1D \rightarrow ^1S$ transitions for selenium and tellurium

at 7247.5 Å and 7909.2 Å. (The recent work of Bowen on the spectra of nebulae makes it clear that the so-called metastable states are nothing but states of long mean life and provided that the gases involved are at sufficiently low pressure, one may expect emission of radiation corresponding to transitions between the levels ordinarily designated as metastable. In such transitions, it will be noted that the azimuthal quantum number selection rules must necessarily be violated).

The line λ 6300 Å would require for its excitation an amount of nearly the same value as in oxygen. We should therefore be able to excite this line also by the collisions of metastable nitrogen atoms in

the active nitrogen with sulphur atoms. Such an experiment, if successful, would not only enable us to locate the exact value of the metastable levels in sulphur and incidentally help us in understanding the structure of the spectrum of sulphur in the Schumann region, but would also provide a convincing test of Kaplan's theory of active nitrogen.

EXPERIMENTAL.

The apparatus employed was practically the same as used by Kichlu and Acharya (*Proc. Roy. Soc.*, 1929, **A**, 123, 168) and in fact similar to that used by most of the investigators on this subject. The nitrogen was taken from a commercial cylinder of compressed gas. It was purified from oxygen and water vapour by passing it over sticks of yellow phosphorus and through tubes containing calcium chloride and phosphorus pentoxide.

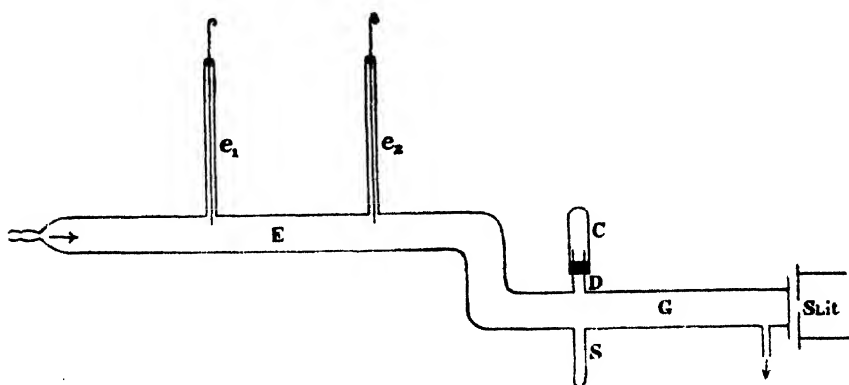


FIG. 1.

The form of the discharge tube used is shown in Fig. 1. A condensed discharge was passed between the electrodes e_1 and e_2 . The direction in which the gas flows is indicated by arrow-heads. The active nitrogen was developed in the tube and was easily recognised by its golden yellow colour. The tube S contained powdered sulphur, which was heated to its boiling point by passing a suitable current through a nichrome wire coil surrounding the tube S. The tube G was also heated similarly to maintain the sulphur in vapourous state, thus ensuring the complete interaction of active nitrogen and sulphur vapour. The position of the slit of the spectrometer is also shown in the figure. The spectrometer

used was "higher constant deviation glass-prism spectrometer" and Ilford special rapid panchromatic plates were used for photography in the region.

Results.

When there was no sulphur in the tube S, the active nitrogen filled the tube G entirely with a golden yellow glow. When, however, sulphur was heated, the tube G was filled with a faint bluish glow, and active nitrogen was faintly visible only in the bend of the discharge tube. The photographs of the spectrum of the bluish glow mentioned above do not show the line $\lambda 6300\text{\AA}$ which is to be expected on Kaplan's theory of active nitrogen. It is possible that the forbidden lines of sulphur are not so easily excited by this method as those of oxygen, although the two are in the same group. We are led to think that Kaplan's postulate regarding the nature of active nitrogen requires further experimental support for its acceptance.

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Synthesis of Chromones. Part I. Condensation of Halogenated Phenols and Cresols with Alkyl Acetoacetic Esters.

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It has been shown by the author (*J. Indian Chem. Soc.*, 1931, 8, 129, 407) that polyhydroxy phenols and α -naphthol readily react with ethyl acetoacetates in presence of sulphuric acid or phosphorus pentoxide to give 1:2-pyrones or coumarins, the latter condensing agent not favouring the formation of 1:4-pyrones or chromones in those cases, as was expected from the experiments of Simonis and his collaborators (*Ber.*, 1913, 46, 2015; 1914, 47, 697, 2220; 1917, 50, 1142). The formation of coumarins with these phenols is instantaneous and is so general that it is difficult to change the course of the reaction even in the case of resorcinol-dimethylether which gives 7-methoxy-4-methylcoumarin with the elimination of the methoxy group.

A perusal of the literature shows that the phenols differ greatly in their degree of readiness to form coumarins using sulphuric acid according to Pechmann. Of the cresols, while *o*-cresol does not react at all, *m*-cresol reacts most readily and the yield of the coumarin from *p*-cresol is not bad. The halogenated phenols respond to this reaction with reluctance, only traces of coumarins being formed (Clayton, *J. Chem. Soc.*, 1908, 93, 2018). It is however possible to change the course of this reaction with these phenols by the application of Simonis method using phosphorus pentoxide which yields chromones. In order to study the effect of substituents in ethyl acetoacetate on this reaction, the cresols and the halogenated phenols have been condensed with unsubstituted and substituted ethyl acetoacetates (the α -substituents being methyl, ethyl, propyl, isopropyl, isobutyl) with interesting results.

The halogenated phenols (*o*-, *p*-chloro- and *o*-, *p*-bromophenols) are by far the best in giving a comparatively good yield of the chromones but the generalisation made by Simonis, that the *o*-substituted phenols give a better yield, seems to be unwarranted. The

effect of the substituents in the acetoacetic ester molecule is not very marked in diminishing or increasing the yield, all giving chromones except ethyl- α -isobutylacetoacetate which gave resinous product from which nothing could be isolated. In the case of cresols it is found that *o*-cresol forms chromones with the alkyl acetoacetic esters with comparatively good yield; *p*-cresol gives a chromone when condensed with ethyl- α -methylacetoacetate but when the substituents are ethyl, propyl or isopropyl, no product can be isolated; *m*-cresol gives a coumarin with unsubstituted acetoacetic ester using both sulphuric acid and phosphorus pentoxide, but with ethyl- α -methylacetoacetate *m*-cresol gives a coumarin in poor yield using sulphuric acid (Kolestermann and Fries, *Annalen*, 1908, 362, 3) and a chromone using phosphorus pentoxide (Petschek and Simonis, *Ber.*, 1913, 46, 2014).

Simonis depended mainly on hydrolytic decomposition to establish the chromone structure of the compounds prepared by him; this often leads however to erroneous results (*cf.* Baker, *J. Chem. Soc.*, 1925, 127, 2349) and in some cases, Simonis himself could not come to definite conclusion due to unsatisfactory hydrolysis. The chromone structure of all the compounds described here have been established by their condensation with aldehydes in presence of sodium ethoxide to form styrene derivatives. The chromones formed by the condensation of phenols with alkyl acetoacetic esters always contain a reactive methyl group in 2-position (*cf.* Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, 123, 2569) and are thus easily distinguished from 4-methylcoumarines as was previously pointed out by the author (*J. Indian Chem. Soc.*, 1931, 8, 131). The present investigation also proves that the reactivity of the 2-methyl group is not in any way influenced by the presence of a group (Cl, Br, or CH_3) in the benzene nucleus as is supposed by Heilbron and others.

EXPERIMENTAL.

General Method of the Preparation of the Halogenated Chromones.

A solution of the halogenated phenol (20 g.) in alkyl acetoacetic ester (19 g.) is slowly added with cooling to phosphorus pentoxide (45 g.) in a flask fitted with a calcium chloride tube, the mass being occasionally stirred. The mixture generally becomes hot and in some cases frothing takes place. After standing for fifteen minutes, it is gradually heated on the water-bath, when the

mass becomes pasty and the colour changes to red. The mixture is then thoroughly mixed and the heating continued for about three hours. The cold sticky product, thus obtained, is then treated with powdered ice and the viscous oil separating is extracted with ether. The ethereal extract is thoroughly washed with 5 p. c. caustic potash solution to remove the unchanged phenol and then with water to remove the alkali. On evaporating the ether a viscous semi-solid product is obtained, which sometimes gives beautiful crystals on washing with petroleum ether but generally, if the semi-solid mass is placed on a porous plate and left overnight, the coloured resinous substances are absorbed and colourless crystals are obtained. The product is finally crystallised from alcohol in a yield of 17 to 30 p. c.

General method of the preparation of the styrene derivatives by condensing the chromones with aldehydes.—An alcoholic solution of sodium ethoxide is added to a solution of the aldehyde (1 mol.) and the chromone (1 mol.) in the minimum quantity of absolute alcohol, when the solution becomes warm. The solution, on keeping overnight, deposits crystals which are filtered off. A further crop of the crystals is also obtained by adding a few drops of water to the alcoholic mother-liquor. On recrystallisation from alcohol or acetic acid, well-defined crystals are obtained in almost quantitative yield.

Chromones from Chlorophenols.

8-Chloro-2-styryl-3-ethylchromone, obtained by the condensation of 8-chloro 2-methyl-3-ethylchromone (from *o*-chlorophenol and ethyl- α -ethylacetoacetate, Simonis and Schuhmann, *Ber.*, 1917, **50**, 1142) with benzaldehyde, crystallises from rectified spirit in silky yellow needles melting at 137°. (Found: Cl, 11.7. $C_{19}H_{15}O_2Cl$ requires Cl, 11.4 per cent.).

8-Chloro-2-methyl-3-propylchromone is obtained in 30 per cent. yield, from *o*-chlorophenol and ethyl- α -propylacetoacetate. It crystallises from alcohol as colourless needles, m.p. 100°. (Found: Cl, 14.72. $C_{13}H_{13}O_2Cl$ requires Cl, 15.0 per cent.).

8-Chloro-2-styryl-3-propylchromone, the condensation product of 8-chloro-2-methyl-3-propylchromone with benzaldehyde, crystallises in needles from rectified spirit, m.p. 109°. (Found: Cl, 10.64. $C_{20}H_{17}O_2Cl$ requires Cl, 10.9 per cent.).

8-Chloro-2-methyl-3-isopropylchromone is prepared by condensing *o*-chlorophenol with ethyl- α -isopropylacetoacetate. The reaction

starts only when heated; no appreciable change takes place in the cold. It crystallises in long shining needles melting at 160° from absolute alcohol. (Found: Cl, 15.3. $C_{13}H_{13}O_2Cl$ requires Cl, 15.4 per cent.).

8-Chloro-2-styryl-3-isopropylchromone, the product obtained by reacting the above chromone with benzaldehyde, crystallises from rectified spirit in fine silky needles melting at 151° . (Found: Cl, 10.58. $C_{20}H_{17}O_2Cl$ requires Cl, 10.9 per cent.).

6-Chloro-2-styryl-3-methylchromone is prepared by the condensation of 6-chloro-2:3-dimethylchromone (from *p*-chlorophenol and ethyl- α -methylacetoacetate) with benzaldehyde. It crystallises from rectified spirit, m.p. 143° . (Found: Cl, 11.5. $C_{18}H_{13}O_2Cl$ requires Cl, 11.9 per cent.).

6-Chloro-2-methyl-3-propylchromone is obtained by condensing *p*-chlorophenol with ethyl- α -propylacetoacetate (the reaction starts in the cold with much rise of temperature). It crystallises from rectified spirit, m.p. 108° . (Found: Cl, 15.26. $C_{13}H_{13}O_2Cl$ requires Cl, 15.0 per cent.).

6-Chloro-2-styryl-3-propylchromone, the condensation product of 6-chloro-2-methyl-3-propylchromone with benzaldehyde, crystallises in needles from alcohol, m.p. 126° . (Found: Cl, 11.3. $C_{20}H_{17}O_2Cl$ requires Cl, 10.9 per cent.).

6-Chloro-2-methyl-3-isopropylchromone, prepared from *p*-chlorophenol and ethyl- α -isopropylacetoacetate, crystallises from rectified spirit, m.p. 127° . (Found: Cl, 14.8. $C_{13}H_{13}O_2Cl$ requires Cl, 15.0 per cent.).

6-Chloro-2-styryl-3-isopropylchromone, obtained by reacting the 6-chloro-2-methyl-3-isopropylchromone with benzaldehyde, crystallises in needles from rectified spirit, m.p., 159° . (Found: Cl, 11.8. $C_{20}H_{17}O_2Cl$ requires Cl, 10.9 per cent.).

6:8-Dichloro-2-styryl-3-ethylchromone is prepared by condensing 6:8-dichloro-2-methyl-3-ethylchromone (from 2:4-dichlorophenol and ethyl- α -ethylacetoacetate) with benzaldehyde. It is crystallised from glacial acetic acid, m.p. $155-57^{\circ}$. (Found: Cl, 21.13. $C_{19}H_{14}O_2Cl_2$ requires Cl, 20.58 per cent.).

Chromones from Bromophenols.

8-Bromo-2-styryl-3-methylchromone, the product of the condensation of 8-bromo-2:3-dimethylchromone (from *o*-bromophenol and ethyl- α -methylacetoacetate) with benzaldehyde, crystallises from

absolute alcohol in silky yellow needles melting at 200° . (Found: Br, 28.71. $C_{13}H_{13}O_2Br$ requires Br, 28.46 per cent.).

8-Bromo-2-methyl-3-propylchromone, prepared from *o*-bromophenol and ethyl- α -propylacetoacetate, is crystallised from rectified spirit, m.p. 82° . (Found: Br, 28.12. $C_{13}H_{13}O_2Br$ requires Br, 28.4 per cent.).

6-Bromo-2-styryl-3-methylchromone, the product obtained by reacting 6-bromo-2:3-dimethylchromone (from *p*-bromophenol and ethyl- α -methylacetoacetate) with benzaldehyde, crystallises in yellow needles melting at 152° from absolute alcohol. (Found: Br, 23.1. $C_{18}H_{13}O_2Br$ requires Br, 23.46 per cent.).

6-Bromo-2-methyl-3-propylchromone, obtained from *p*-bromophenol and ethyl- α -propylacetoacetate, crystallises from dilute alcohol, m.p. 112° . (Found: Br, 28.5. $C_{13}H_{13}O_2Br$ requires Br, 28.4 per cent.).

6-Bromo-2-styryl-3-propylchromone, is crystallised from rectified spirit, m.p. 129° . (Found: Br, 21.2. $C_{20}H_{17}O_2Br$ requires Br, 21.6 per cent.).

Chromones from Cresols.

2-Styryl-3:6-dimethylchromone is obtained by condensing 2:3:6-trimethylchromone (from *p*-cresol and ethyl- α -methylacetoacetate, Petscheck and Simonis, *loc. cit.*) with benzaldehyde. It crystallises from rectified spirit as hard crystals melting at 120° . (Found: C, 82.48; H, 6.0. $C_{19}H_{16}O_2$ requires C, 82.60; H, 5.8 per cent.).

3:4:6-Trimethylcoumarin, isomeric with 2:3:6-trimethylchromone is obtained by adding sulphuric acid (20 c.c.) in the cold to a solution of *p*-cresol (4 g.) in ethyl- α -methylacetoacetate (5 g.), keeping overnight and pouring the solution into water. It crystallises from dilute alcohol as colourless prisms, m.p. 165° , yield 5 g. (Found: C, 76.65; H, 6.48. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4 per cent.).

2-Styryl-3:8-dimethylchromone, prepared by reacting 2:3:8-trimethylchromone (from *o*-cresol with ethyl- α -methylacetoacetate, Petscheck and Simonis, *loc. cit.*) with benzaldehyde, crystallises as fine needles melting at 138° from rectified spirit. (Found: C, 82.55; H, 5.51. $C_{19}H_{16}O_2$ requires C, 82.60; H, 5.8 per cent.).

2-(*m*-nitro-)styryl-3:8-dimethylchromone is produced by condensing 2:3:8-trimethylchromone with *m*-nitrobenzaldehyde. Silky needles (m.p. 225°) from glacial acetic acid. (Found: N, 4.56. $C_{19}H_{15}O_4N$ requires N, 4.86 per cent.).

2:8-Methyl-3-ethylchromone, prepared by the interaction of *o*-cresol with ethyl- α -ethylacetoacetate, crystallises from dilute alcohol, m.p. 71-72°. (Found: C, 77.1; H, 7.2. $C_{13}H_{14}O_2$ requires C, 77.22; H, 6.9 per cent.).

2-Styryl-8-methyl-3-ethylchromone, the condensation product of the above chromone with benzaldehyde, crystallises from rectified spirit, m.p. 142°. (Found: C, 82.91; H, 6.05. $C_{20}H_{18}O_2$ requires C, 82.75; H, 6.2 per cent.).

Coumarins from Resorcinol-mono- and dimethylether.

7-Methoxy-4-methylcoumarin.—(a) Resorcinol-monomethylether (5 g.) is condensed with ethyl acetoacetate (5 g.) with sulphuric acid (15 c.c.) in the cold. The reaction mixture, on keeping overnight, is poured into ice-cold water and the precipitate collected and crystallised as rhombic plates from dilute alcohol, m.p. 156-57°.

When phosphorus pentoxide (30 g.) is added in the cold to a solution of resorcinol-monomethylether (5 g.) and ethyl acetoacetate (5.5 g.) vigorous reaction takes place. The mixture is poured into water and the solid collected and crystallised. It also melts at 156-57°, no depression of the melting point taking place when mixed with a specimen of the compound prepared with sulphuric acid or with a specimen of the methoxy derivative of β -methylumbelliferone.

(b) To a solution of resorcinol-dimethylether and ethyl acetoacetate sulphuric acid is added drop by drop at 0° (otherwise effervescence takes place and resinous products obtained). On keeping overnight and pouring into water a red solid is obtained. It is purified by heating on the water-bath with 10 p. c. caustic potash and acidifying. The precipitate, is collected, washed with sodium bicarbonate solution and crystallised from dilute alcohol, m. p. 156-57°, no depression was observed when mixed with 7-methoxy-4-methylcoumarin.

My grateful thanks are due to Prof. R. N. Sen for his keen interest in this investigation, to Dr. J. C. Bardhan for valuable advice and to Dr. P. Neogi for advice and facilities for conducting this work in his laboratory.

Synthesis of Chromones. Part II. Condensation of Nitrophenols with Alkyl Acetoacetic Esters.

BY DUHKHAHARAN CHAKRAVARTI.

In order to find a satisfactory explanation of the causes of Simonis synthesis of chromones from phenols and alkyl acetoacetic esters using phosphorus pentoxide as the condensing agent, the reaction has been extended to nitrophenols and phenol carboxylic acids. It is remarkable that phenols possessing a negative substituent such as NO_2 and COOH which do not respond at all to Pechmann's reaction (Clayton, *J. Chem. Soc.*, 1908, 93, 2108; Pechmann, *Ber.*, 1899, 32, 3881), produce chromones, though with extremely poor yield, when condensed with the alkyl acetoacetic esters by means of phosphorous pentoxide. The nitrochromones are described in this paper, while the chromone-carboxylic acids will form the subject of the next communication.

The nitrophenols react with the alkyl acetoacetic esters with explosive violence and deeply coloured resinous products are invariably formed. Of the three nitrophenols, *m*-nitrophenol gives the best yield. The nitrochromones derived from *m*-nitrophenol may be 5- or 7-nitro-compounds and as attempts to establish the constitution by hydrolytic decomposition have not been successful, they are now provisionally described as 7-nitro-compounds. With *o*-nitrophenol no product could be isolated but it is desired to repeat the condensation using solvents.

These nitrochromones contain a reactive methyl group in 2-position and hence can readily be condensed with the aldehydes in presence of alcoholic sodium ethoxide and are thereby distinguished from the isomeric 4-methylcoumarins. The presence of a nitro group does not in any way lower the reactivity of the methyl group.

The work continued by the author in this line leads to the following conclusions:—

(1) *Pechmann's reaction*.—If the phenol reacts with a β -ketonic ester in presence of sulphuric acid, it will form always a

coumarin, any α -substituent in the acetoacetic ester molecule having no effect in the case of resorcinol, orcinol, pyrogallol, phloroglucinol and α -naphthol, which always show a marked tendency to form coumarins with good yield. *P*- and *m*-cresols form coumarins with unsubstituted acetoacetic ester, but with substituted ester the yield diminishes and no reaction takes place when substituents are heavy such as, propyl, isopropyl and isobutyl, due probably to the non-enolisation of the esters. *o*-Cresol, nitrophenols and phenol-carboxylic acids do not react at all.

(2) *Simonis reaction*.—By using phosphorus pentoxide in place of sulphuric acid, phenols (*e.g.*, resorcinol, orcinol, pyrogallol, phloroglucinol, α -naphthol) which form coumarins readily with good yield using sulphuric acid, invariably give coumarins. Phenols, which react with difficulty to form coumarins (*e.g.*, phenol, *p*-cresol, halogenated phenols) or do not react all (*e.g.*, *o*-cresol, nitrophenols, phenol-carboxylic acids, guaiacol, hydroquinone) using sulphuric acid as the condensing agent, yield with phosphorus pentoxide chromones. *m*-Cresol reacts with ethyl acetoacetate to form coumarin in good yield with sulphuric acid, and it also forms coumarin with phosphorus pentoxide; but with substituted acetoacetic ester, *m*-cresol does not give a good yield of coumarin using sulphuric acid and so it forms a chromone with substituted acetoacetic ester in presence of phosphorus pentoxide.

The theoretical discussion regarding these reactions is reserved until further work.

EXPERIMENTAL.

General Method of the Preparation of the Nitrochromones.

Phosphorus pentoxide (25 g.) is gradually added with stirring to a well-cooled solution of the nitrophenol (20 g.) in the alkyl acetoacetic ester (10g.) and the mixture is very slowly warmed up to 60-70° when it gradually becomes pasty and frothing takes place. It is then heated on the boiling water-bath for about 1½ hours. If this initial heating be not slow and gradual, the reaction sets in with explosive violence and the temperature rises so much that the whole mass is charred especially in the case of *p*-nitrophenol. Phosphorus pentoxide (15-20g.) is again added to the deeply coloured mass and the heating continued for an hour more to ensure complete reaction. The cold product is then treated with ice-cold water and the black product extracted with ether. The ethereal extract is carefully

washed with 5 p.c. caustic potash solution to dissolve the unaltered nitrophenol and then with water to remove the excess of alkali. As the ether evaporates off, shining crystals of the chromone separate out, which are filtered off, washed with a little alcohol to remove the adhering oily impurities and finally crystallised from absolute alcohol. The nitrochromones are mostly sparingly soluble in alcohol and ether.

General method of the preparation of the styryl derivatives by the condensation of the nitrochromones with aldehydes.—The method is the same as that of Heilbron, Barnes and Morton (*J. Chem. Soc.*, 1923, 123, 2569). The nitrostyrene derivatives are coloured yellow to brown and are highly insoluble compounds.

Chromones from p-Nitrophenol.

6-Nitro-2:3-dimethylchromone is prepared by condensing *p*-nitrophenol with ethyl- α -methylacetoacetate. It crystallises from absolute alcohol as shining prisms melting at 163° and is identical with the chromone prepared by Petschek and Simonis (*Ber.*, 1913, 46, 2014) by the nitration of 2:3-dimethylchromone. (Found: N, 6.6. $C_{11}H_9O_4$ N requires N, 6.39 per cent.).

6-Nitro-2-styryl-3-methylchromone, the condensation product of 6-nitro-2:3-dimethylchromone with benzaldehyde, crystallises from glacial acetic acid as yellow needles melting at 205° . (Found: N, 4.8. $C_{18}H_{13}O_4$ N requires N, 4.56 per cent.).

6-Nitro-2-methyl-3-ethylchromone is obtained by the interaction of *p*-nitrophenol with ethyl- α -ethylacetoacetate. It is sparingly soluble in ether and crystallises in needles from absolute alcohol, m.p. 184° . (Found: N, 6.4. $C_{12}H_{11}O_4$ N requires N, 6.0 per cent.).

6-Nitro-2-styryl-3-ethylchromone, prepared by condensing the chromone with benzaldehyde, crystallises in yellow needles from glacial acetic acid, m.p. 239° . (Found: N, 4.1. $C_{19}H_{15}O_4$ N requires N, 4.36 per cent.).

6-Nitro-2-methyl-3-propylchromone is prepared from *p*-nitrophenol and ethyl- α -propylacetoacetate. It is very much soluble in ether and is finally crystallised in long needles from rectified spirit, m.p. 125° . (Found: N, 5.9. $C_{13}H_{13}O_4$ N requires N, 5.66 per cent.).

6-Nitro-2-methyl-3-isobutylchromone, the condensation product of *p*-nitrophenol with ethyl- α -isobutylacetoacetate, crystallises from

rectified spirit in long needles melting at 96° . In this case an appreciable amount of black residue remains, which is insoluble in ether. (Found: N, 5.8. $C_{14}H_{15}O_4$ N requires N, 5.36 per cent.).

Chromones from m-Nitrophenol.

7-Nitro-2:3-dimethylchromone is prepared by condensing *m*-nitrophenol with ethyl- α -methylacetoacetate. The reaction is vigorous in this case. It is crystallised from absolute alcohol in needles melting at 136° . (Found: N, 6.5. $C_{11}H_9O_4$ N requires N, 6.39 per cent.).

7-Nitro-2-styryl-3-methylchromone, the product of condensation of *7-nitro-2:3-dimethylchromone* with benzaldehyde crystallises from glacial acetic acid in yellow needles melting at 258° . (Found: N, 4.8. $C_{18}H_{13}O_4$ N requires N, 4.56 per cent.).

7-Nitro-2-methyl-3-ethylchromone, prepared from *m*-nitrophenol and ethyl- α -ethylacetoacetate, crystallises in needles from absolute alcohol, m.p. 167° . (Found: N, 5.8. $C_{12}H_{11}O_4$ N requires N, 6.0 per cent.).

7-Nitro-2-methyl-3-propylchromone, obtained from *m*-nitrophenol and ethyl- α -propylacetoacetate, is crystallised from rectified spirit, m. p. 136° . (Found: N, 5.72. $C_{13}H_{13}O_4$ N requires N, 5.66 per cent.).

7-Nitro-2 (m-nitro)-styryl-3-propylchromone is prepared by condensing the above chromone with *m*-nitrobenzaldehyde. It crystallises from a large volume of glacial acetic acid, m.p. 256° . (Found: N, 7.23. $C_{20}H_{16}O_6N_2$ requires N, 7.36 per cent.).

7-Nitro-2-methyl 3-isopropylchromone, prepared from *m*-nitrophenol and ethyl- α -isopropylacetoacetate, crystallises from rectified spirit in needles melting at 133° . (Found: N, 5.74. $C_{13}H_{13}O_4$ N requires N, 5.66 per cent.).

7-Nitro-2 (m-nitro)-styryl-3-isopropylchromone, the condensation product of *7-nitro-2-methyl-3-isopropylchromone* with *m*-nitrobenzaldehyde, crystallises from a large volume of glacial acetic acid, as light yellow needles which do not melt up to 270° . (Found: N, 7.61. $C_{20}H_{16}O_6N_2$ requires N, 7.36 per cent.).

7-Nitro-2-methyl-3-isobutylchromone, prepared from *m*-nitrophenol and ethyl- α -isobutylacetoacetate, is crystallised from rectified spirit, m.p. 158° . (Found: N, 5.44. $C_{14}H_{15}O_4$ N requires N, 5.86 per cent.).

7-Nitro-2 (m-nitro)-styryl-3-isobutylchromone, obtained by condensing 7-nitro-2-methyl-3-isobutylchromone with *m*-nitrobenzaldehyde, is crystallised from glacial acetic acid, m.p. 252°. (Found: N, 7.23. $C_{21}H_{18}O_6N_2$ requires N, 7.1 per cent.).

My grateful thanks are due to Prof. R. N. Sen for his keen interest in this investigation, to Dr. J. C. Bardhan for valuable advice and to Dr. P. Neogi for advice and facilities for conducting this work in his laboratory.

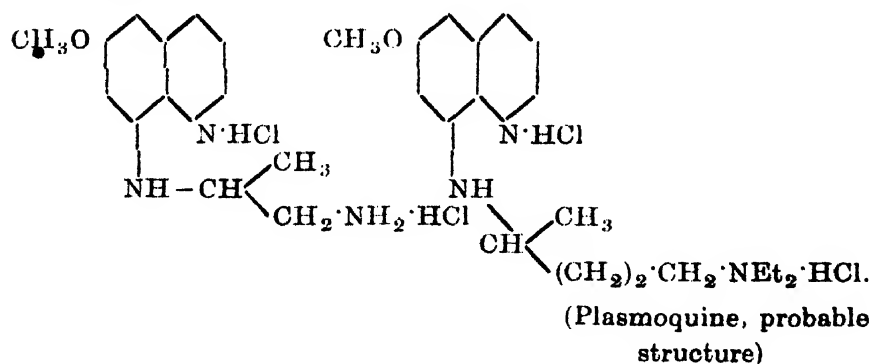
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Studies in Quinoline Compounds. Part VI.

By UPENDRANATH BRAHMACHARI AND JNANENDRA MOHAN DAS-GUPTA.

The first series of compounds investigated in the following paper are alkylaminoquinoline derivatives which bear close relationship to plasmoquine type of compounds. The general contour is very similar; while position 8 is occupied by amino group, position 6 is occupied by a methoxy, ethoxy or chloro group. Further attachment of an alkylamino group to the former makes the general structure akin to that usually ascribed to plasmoquine, the constitution of which, however, is not definitely known. The object of preparing these compounds is, therefore, to approach the constitution of plasmoquine in a systematic way. The similarity of the compounds investigated with plasmoquine will be apparent from the following structures.

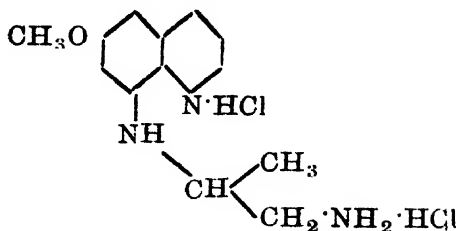


It will be noticed that the alkylaminoquinolines prepared by us contain asymmetric carbon atoms which are also present in plasmoquine and quinine.

The second series of compounds are characterised by having unsaturated linkages (attached to the amino group in position 8), which are also present in quinine though not in plasmoquine.

In all cases the hydrochlorides have been prepared as these are more easily crystallised than the corresponding bases; moreover, the bases are insoluble in water while the hydrochlorides are readily soluble and are so well adapted for pharmacological experiments.

EXPERIMENTAL.

*First Series.**6-Methoxy-8-β-aminoisopropylaminoquinoline Dihydrochloride.*

The preparation of this compound is given here in greater detail than in our previous paper (*J. Indian Chem. Soc.*, 1931, **8**, 571). The starting materials for the synthesis of this compound are 6-methoxy-8-aminoquinoline and β -bromoisopropylphthalimide. The former is prepared by nitrating acetyl-*p*-anisidine and subsequent hydrolysis of the acetyl group.

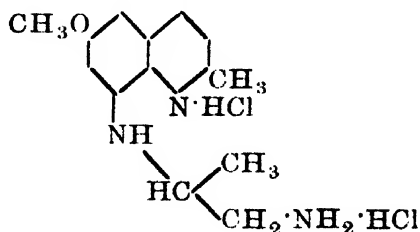
The amino compound thus obtained is then subjected to Skraup's reaction which gives 6-methoxy-8-aminoquinoline (British Pat., 267, 169). This is then condensed with β -bromoisopropylphthalimide. This latter is obtained by condensing phthalic anhydride with allylamine and then warming the resulting allylphthalimide with fuming HBr or alternately by condensing allyliodide with potassium phthalimide and then proceeding as above (*cf.* Seitz, *Ber.*, 1891, **24**, 2624).

6-Methoxy-8-aminoquinoline (1 g.) and bromoisopropylphthalimide (2 g.) are boiled together in an oil-bath at 130° for about 6 hours at the end of which the mass solidifies. The product is then treated with alcohol which dissolves the excess of bromopropylphthalimide and aminoquinoline, while the hydrobromide of phthalimidoisopropylaminomethoxyquinoline remains insoluble. It is then filtered, washed with alcohol and dried. As it is difficult to hydrolyse it, its hydrazine condensation product is prepared, which can be easily hydrolysed (*cf.* Ing and Muske, *J. Chem. Soc.*, 1926, p. 2348).

The hydrobromide (5 g.) is treated with alcohol (3 c.c.) and hydrazine hydrate (0.1 c.c.) next added. The whole is refluxed for 1½ hours and alcohol is distilled off while a white spongy mass remains. This latter is then hydrolysed by warming for about 15 minutes on a water-bath with excess of dilute hydrochloric acid. The

mixture is filtered, the filtrate is made alkaline and the precipitated base is extracted with chloroform. The chloroform solution is then treated with HCl gas, when the dihydrochloride is obtained. This is purified from alcohol in yellow crystalline form melting at 218-20°. It readily dissolves in water to a clear yellow solution. (Found: N, 13.70; Cl, 23.30. $C_{13}H_{19}ON_3Cl_2$ requires N, 13.81; Cl, 23.35 per cent.).

2-Methyl-6-methoxy-8-β-aminoisopropylaminoquinoline Dihydrochloride.



It is obtained similarly from 2-methyl-6-methoxy-8-aminoquinoline which is prepared by applying Doebner and Miller's reaction to 4-methoxy-2-nitroaniline and subsequent reduction. It is a yellow crystalline compound which melts at 260°. (Found: N, 13.30; Cl, 22.20. $C_{14}H_{21}ON_3Cl_2$ requires N, 13.34; Cl, 22.33 per cent.).

2-Methyl-6-ethoxy-8-β-aminoisopropylaminoquinoline dihydrochloride.—It is obtained from 2-methyl-6-ethoxy-8-aminoquinoline which results from Doebner and Miller's reaction on the corresponding nitroaniline and subsequent reduction. It melts at 270°. (Found: N, 12.70; Cl, 21.42. $C_{15}H_{23}ON_3Cl_2$ requires N, 12.65; Cl, 21.38 per cent.).

6-Chloro-8-β-aminopropylaminoquinoline dihydrochloride.—It is obtained as before from 6-chloro-8-aminoquinoline. It is a yellow crystalline compound melting at 212°. (Found: N, 13.50; Cl, 34.41. $C_{12}H_{16}N_3Cl_3$ requires N, 13.61; Cl, 34.52 per cent.).

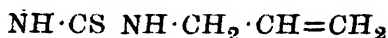
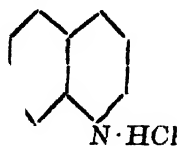
2-Methyl-6-chloro-8-β-aminoisopropylaminoquinoline dihydrochloride.—It is obtained as above from 2-methyl-6-chloro-8-aminoquinoline. It melts at 255°. (Found: N, 13.1; Cl, 33.1. $C_{13}H_{18}N_3Cl_3$ requires N, 13.02; Cl, 33.02 per cent.).

2-Methyl-8-β-aminoisopropylaminoquinoline dihydrochloride.—It is prepared similarly from 2-methyl-8-aminoquinoline. It melts at

275-80°. (Found: N, 14.50; Cl, 24.42. $C_{13}H_{19}N_3Cl_2$ requires N, 14.58; Cl, 24.65 per cent.).

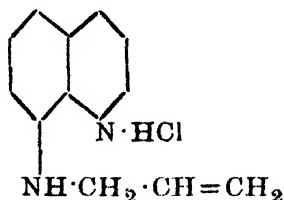
Second Series.

Allylthiocarbamido-8-aminoquinoline Hydrochloride.

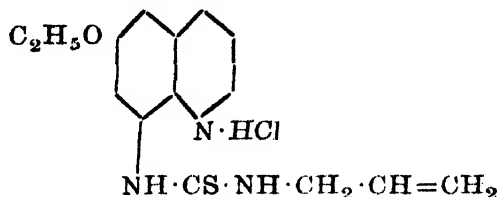


Aminoquinoline (1 g.) is mixed with allylisocyanate (1 g.) in methyl alcohol (5 c.c.). The mixture is warmed on water-bath for sometime and then poured into water. The precipitate is dissolved in hydrochloric acid, shaken with ether and the aqueous solution is made alkaline. The precipitate obtained is taken up with chloroform and the hydrochloride precipitated therefrom by passing HCl gas. It crystallises from alcohol and melts at 150°. It forms a yellow crystalline chromate with $K_2Cr_2O_7$ which does not melt below 300°. (Found: N, 15.20; Cl, 12.61. $C_{13}H_{14}N_3SCl$ requires N, 15.02; Cl, 12.70 per cent.).

Allyl-8-aminoquinoline Hydrochloride.

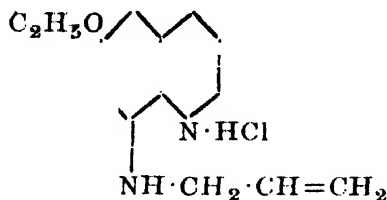


8-Aminoquinoline (1 g.) and allylbromide (1 g.) are mixed with Na_2CO_3 (2 g.) dissolved in 10 c.c. of water. The whole is refluxed for three hours. The mixture is shaken with ether and the hydrochloride is precipitated from the ethereal solution by passing HCl gas. It crystallises from alcohol, m.p. 175°. It gives with potassium dichromate solution a chromate which does not melt below 300°. (Found: N, 12.8; Cl, 11.50. $C_{12}H_{13}N_2Cl$ requires N, 12.7; Cl, 11.56 per cent.).

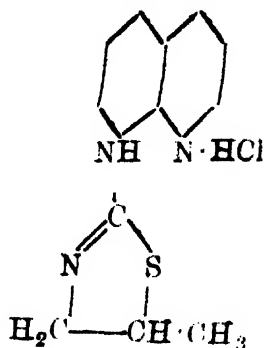
Allylthiocarbamido-8-amino-6-ethoxyquinoline Hydrochloride.

The starting materials in the preparation of this compound are 6-ethoxy-8-aminoquinoline and allylthiocyanate. The former is obtained by reducing 6-ethoxy-8-nitroquinoline with SnCl_2 and conc. HCl , the nitroquinoline derivative itself being obtained by applying Skraup's reaction to 4-ethoxy-2-nitroaniline (*loc. cit.*).

6-Ethoxy-8-aminoquinoline (2 g.) and an equivalent amount of allylthiocyanate in 10 c.c. of methyl alcohol are warmed together on water bath for about an hour. The mixture is poured into water and purified as in the case of allylthiocarbamido-8-aminoquinoline. The hydrochloride is produced by passing dry HCl gas through its ethereal solution. It melts at 160° and forms a yellow dichromate which does not melt below 300° . (Found: N, 13.10; Cl, 11.10; $\text{C}_{15}\text{H}_{18}\text{ON}_3\text{S}\text{Cl}$ requires N, 12.98; Cl, 10.97 per cent.).

Allyl-8-amino-6-ethoxyquinoline Hydrochloride.

It is prepared by refluxing a mixture of 6-ethoxy-8-aminoquinoline (1 g.), allylbromide (1.1 g.) and Na_2CO_3 (2 g.) dissolved in 8–10 c.c. of water. The refluxing is continued for 2 to 3 hours. It is then cooled and treated with ether. The hydrochloride is prepared as in the case of allyl-8-aminoquinoline; m.p. 182° . It forms a crystalline dichromate, which does not melt below 300° . (Found: N, 10.58; Cl, 13.32. $\text{C}_{14}\text{H}_{17}\text{ON}_2\text{Cl}$ requires N, 10.59; Cl, 13.42 per cent.).

N-(8-quinolyl)- μ -Amino- α -methylthiazoline Hydrochloride.

It is prepared by warming allylthiocarbamido-8-aminoquinoline with excess of concentrated hydrobromic acid on water-bath for about an hour. The mixture is cooled and diluted with water and then made alkaline with caustic soda solution. The precipitate is next extracted with ether. The ethereal solution is dried over anhydrous K_2CO_3 , and the hydrochloride prepared as usual. It melts at $215-20^\circ$ (decomp.). It is a light yellow substance and dissolves with difficulty in water to a light yellow solution. (Found: N, 15.00; Cl, 12.62. $C_{13}H_{14}N_3SCl$ requires N, 15.02; Cl 12.70 per cent.).

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Studies in Oxidation-Reduction Potential. Part I. Cystine.

BY J. C. GHOSH, S. N. RAYCHAUDHURI AND S. C. GANGULI.

The discovery of glutathione by Hopkins (*Biochem. J.*, 1921, 15, 286) in all living tissues and the probability of this substance acting as a carrier of oxygen has naturally directed the attention of investigators to the properties and behaviour of sulphhydryl bodies. Glutathione contains cysteine as one of its constituent parts and obviously the study of oxidation-reduction potential of cysteine has great significance in the study of tissue oxidation. Now, if the oxidation-reduction of cysteine according to the following scheme:—



were truly reversible, and a thermodynamic equilibrium existed at the noble electrodes, the value of electrode potential would be given by

$$E = E_0 - \frac{RT}{F} p_{\text{H}} - \frac{RT}{F} \log \frac{[\text{cysteine}]}{\sqrt{[\text{cystine}]}} \quad \dots (1)$$

Dixon and Quastel (*J. Chem. Soc.*, 1923, 123, 2943) and later on Michaelis and his co-workers (Michaelis and Flexner, *J. Biol. Chem.*, 1928, 79, 689 ; Barron, Flexner and Michaelis, *ibid.*, 1929, 81, 743) have carefully studied the reduction potential developed by solutions of cysteine at gold and mercury electrodes and found the following equation to hold good.

$$E = E_0 - \frac{RT}{F} p_{\text{H}} - \frac{RT}{F} \log [\text{cysteine}]. \quad \dots (2)$$

Strangely enough they found that the addition of cystine has no influence on this electrode potential, and Barron, Flexner and Michaelis (*loc. cit.*), state "It is improper to speak of a cystine—cysteine system at a mercury electrode.....This system is not related to the problem of cysteine oxidation in metabolism."

This is a very unsatisfactory position, and further investigation appeared very desirable. The previous investigators brought a buffered solution of cysteine and cystine hydrochloride in contact with a noble metal under anaerobic conditions and the potential developed referred to the normal hydrogen electrode was found to be given by equation (2) where E_0 has the value -0.001 volt.

Now, if the potential is due to the oxidation of cysteine, it ought to be of the same order of magnitude as is necessary for the reduction of cystine. This point could be tested by determining the overvoltage at the cathode necessary for the reduction. Table I gives the potential we have found to be necessary for the reduction of cystine.

The experimental arrangement consisted of two glass beakers containing the same solution of cystine hydrochloride connected by means of a siphon. One beaker contained ring-shaped anode of platinum gauze and the other a large piece of platinum, silver, copper foil or mercury as cathode. A stirrer rapidly stirred the liquid at the cathode and the overvoltage was determined by means of a Wolff potentiometer against a decinormal calomel electrode.

The cystine and cysteine in the cathode liquid was estimated colorimetrically according to Folin and Marenzi (*J. Biol. Chem.*, 1929, **83**, 103) with slight modification. 4 C.c. of the cathode liquid was pipetted out and transferred to a 100 c.c. volumetric flask and 2 c.c. of a standard solution of cystine (containing 1 μ g. per c.c. in *N*-sulphuric acid) to another 2 c.c. of a freshly prepared 20 p.c. solution of sodium sulphite was added to the standard cystine solution for its reduction and allowed to stand for a minute. 18 C.c. of 20 p.c. sodium carbonate was then added to each flask. After the addition of carbonate solution, 2 c.c. of 20 p.c. lithium sulphate was added to each flask and finally 8 c.c. of uric acid reagent was added to each flask with shaking. In the case of the standard, the solution was made up to a definite volume with a freshly prepared 3 p.c. solution of sodium sulphite, and with deaerated water in the other case. The strength was then determined colorimetrically.

TABLE I.

p_H .	Current density.	Electrode.	Cathode potential against <i>N</i> -hydrogen Electrode.	Extent of reduction.
3.2	1.46×10^{-4}	Mercury	-0.7588	Measurable in 3 hrs
"	2.09×10^{-4}	"	-0.7696	Complete in 3 hrs. *
"	3.20×10^{-4}	Copper	-0.4441	Very small in 3 hrs.
"	3.84×10^{-4}	"	-0.4442	47.06% in 3 hrs.
"	"	"	-0.4445	70.2% in $6\frac{1}{2}$ hrs.
"	3.13×10^{-4}	Silver	-0.4407	49.4% in 3 hrs.
"	"	"	-0.4489	86.98% in 3 hrs.
"	5.20×10^{-4}	Platinum	-0.3520	None in 3 hrs.
"	"	"	"	None in 6 hrs.
"	1.04×10^{-3}	"	-0.4205	22.4% in $3\frac{1}{2}$ hrs.
"	7.81×10^{-4}	"	-0.4086	24% in 5 hrs.
"	"	"	-0.4186	39.2% in $7\frac{1}{2}$ hrs.
7.0	1.98×10^{-4}	Mercury	-0.9109	Complete in 3 hrs.

It is well known that the direct method used above and the commutator method advocated by Newbury, give different over voltage values. The former method gives invariably higher values. There is at the present time no unanimity of opinion as to which method gives the correct value. The data in Table I have therefore no quantitative significance. One important fact however should be noted; on a platinum surface hydrogen discharged at current density 1×10^{-3} can reduce cystine to cysteine. at p_H 0.3, but not at lower densities. It is clear that the cystine-cysteine potential cannot be far removed from that of the potential developed in a hydrogen gas cell.

While the investigation was in progress two papers (Williams and Drissen (*J. Biol. Chem.*, 1930, **87**, 441) and the other by Fischer, *J. Biol. Chem.*, 1930, **89**, 753) were published in which the problem has been treated differently. Cysteine was oxidised to cystine by oxidising agents (I_2 , KIO_3 , $K_2Cr_2O_7$ etc.) and attempts were made

to locate the redox potential by electrometric titration. The normal potential varied from +415 to +548 volt depending on the oxidising agents. A positive potential at the cathode of the observed magnitude should certainly be incapable of reducing cystine to cysteine. Williams and Drissen consider that in the electrometric titrations, one minute was sufficient for the attainment of equilibrium. This assumption is perhaps not correct, and what they actually recorded, may, for example in the case of iodine as oxidising agent, be the 'redox' potential of the system $I_2 \rightleftharpoons 2I'$, the actual value of the potential depending on the concentrations of the I' ion and the small concentrations of I_2 that may exist in the solution at the end of one minute.

From the qualitative knowledge of the negative potential necessary for the reduction of cystine to cysteine, a method for finding out accurately the redox potential was worked out as follows:

Under perfectly anaerobic conditions, cystine was partly converted to cysteine by cathodic reduction at a mercury electrode. The electrolysing current was then switched off, and the negative potential determined from time to time while a current of nitrogen was continually flowing. Under these conditions, we would expect to observe a limiting value of the potential corresponding to the cystine-cysteine redox system. This expectation was realised when the p_H value was 7 and more. For lower p_H values erratic results were obtained. It is remarkable that the limiting values of the *E.M.F.* observed for p_H values 7 or more are capable of being expressed by equation (1) where E_0 is found to have the value 0.0793.

Also for the same p_H , the variation in the *E.M.F.* with changes in the cystine-cysteine ratio follows the relation—

$$E_1 - E_2 = RT/F \log \frac{[\text{cystine}]_1 \sqrt{[\text{cystine}]_2}}{\sqrt{[\text{cystine}]_1} [\text{cystine}]_2} \quad \dots (3)$$

$E_1 - E_2$ is not given by the following relation

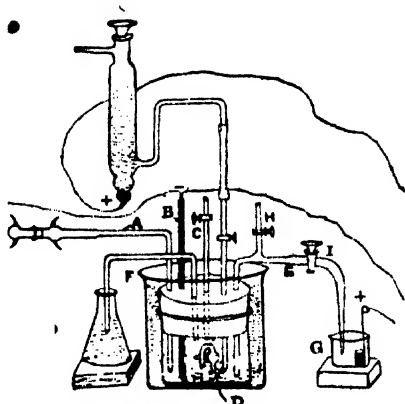
$$E_1 - E_2 = RT/F \log [\text{cystine}]_1 / [\text{cystine}]_2 \quad \dots (4)$$

as demanded by the equation of Dixon and Quastel.

In solutions of a substance like cysteine, the slightest trace of oxygen has a great effect on the potential. The most important

feature of the experimental technique was therefore to remove the oxygen as completely as possible from the cystine-cysteine mixture. This involved the supply of carefully purified nitrogen and an efficiently sealed apparatus. Nitrogen prepared from ammonium chloride and sodium nitrite was stored up in a jar and further purified by allowing it to flow up a tower packed with copper turnings which were kept moist throughout with a mixture of equal volumes of saturated ammonium carbonate solution and liquor ammonia ($d\ 0.93$). The issuing gas was then passed successively through three towers containing

FIG. 1.



alkaline pyrogallate solution, dilute sulphuric acid solution and concentrated sulphuric acid respectively. A piece of white phosphorus did not glow in the issuing gas showing that the oxygen pressure was less than 0.0007 mm. This gas was finally allowed to enter the cell. All connections from the gas reservoir to the cell were made of glass tubing. The cell was made out of a glass bottle of suitable size and had a capacity of about 150 c.c. This was fitted with a rubber stopper in which six holes were bored at equal distances from one another. The following glass tubes were inserted in the bores for the purpose mentioned below:—

(i) A is the nitrogen inlet with a ground-glass joint. The lower end of the tube nearly touches the surface of mercury inside the cell.

(ii) F is the nitrogen outlet. Its outer end dips in water to serve as a trap.

(iii) B is a glass tube at the lower end of which is fused a platinum wire in order to make an electrical connection with the mercury within the cell. Enough mercury should be taken within the cell to immerse the wire completely.

(iv) C is a stop-cock large enough to allow the passage of a 2 c.c. pipette. This was used for the introduction of the solution within the cell as well as for withdrawal of solution from the cell for analysis.

(v) E is a siphon-tube with two stop-cocks H and I for making liquid connection with the anode chamber. The stop-cock I is on the main body of the siphon and is of considerable diameter so that it offers only a small resistance. When the electrolysing current is switched off, the stop-cock is also closed in order to prevent any back rush of the liquid from the anode chamber to the cathode chamber where obviously the pressure will fall due to the bubbling of nitrogen at a slower rate.

(vi) D is an arrangement for making connection with the decinormal calomel electrode. It is filled up with saturated potassium chloride.

G is the anode chamber. The anode used is a platinum gauze ring. A wire resistance was inserted between the poles of a battery of cells and the required voltage for electrolysis was applied by tapping off the current from the resistance. The cell fitted as stated above was made airtight with marine glue, soft sealing wax and a final coating of paraffin wax. It was then completely immersed in a bath of liquid paraffin in order to exclude the last traces of air from entering. The nitrogen reservoir was connected at the ground glass part of A and a decinormal calomel electrode was connected at D. A regular stream of nitrogen helped to stir the liquid.

The hydrogen-ion concentration was kept practically constant by means of buffer solutions; the cystine-cysteine ratio was varied by continual reduction at the cathode under perfectly anaerobic conditions for different lengths of time.

Cystine, dissolved in the least quantity of hydrochloric acid was added to the buffer solution to bring it to the desired concentration. Due to the addition of hydrochloric acid in the cystine solution, the p_H value of the buffer solution was diminished by about 0.6 units every time. The p_H value of cystine solution in each case was therefore determined electrometrically.*

Cystine solution thus prepared was introduced into the electrolytic cell and a portion of it into the anode chamber. The potentials were measured against a 0.1N—calomel electrode. While the reduction was in progress, the nitrogen was bubbled more rapidly

* The value of p_H obtained electrometrically may not be absolutely correct as cystine react as a powerful reducing agent. As a matter of fact, however, the colorimetric method gave values of p_H similar to those obtained by the electrometric method. For the verification of reaction (4) the absolute value of p_H is not also essential.

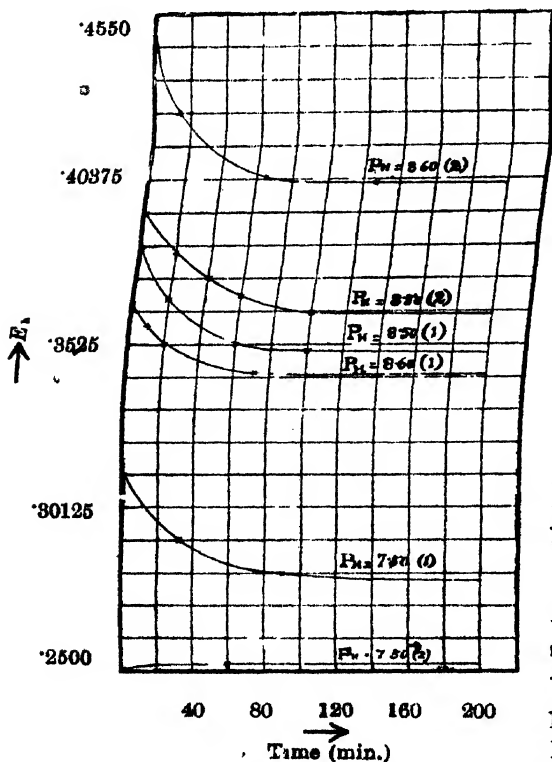
to secure an efficient stirring. But after switching off the current, the potential was read with the nitrogen passing slowly and at an approximately regular rate through the electrolytic cell. Small variations in the rate of bubbling are without effect on the steady *E.M.F.*.

After the attainment of the steady state, more cystine was reduced electrolytically (5 milliamperes for $\frac{1}{2}$ hour) as before, and the measurements continued. After each reduction, 2 c.c. of the cathode solution was taken out and the amount of cystine in the mixture determined colorimetrically.

Pfansteil's C. P. cystine was purified by dissolving several times in very dilute caustic soda solution and then precipitating with dilute acetic acid. 2 C.c. of the cystine solution was added to 80 c.c. buffer solution to bring it to the desired concentration.

Mercury used as cathode was carefully purified. All experiments

FIG 2



were done at 25° and when the experiment was over, sulphuretted hydrogen was passed through the cathode liquid, but it failed to produce any precipitate showing that in the cathode no complex of cystine and mercury had been formed.

Table II shows the limiting potentials in volts referred to the normal hydrogen electrode for p_H values above 7. Fig. 2 illustrates the rate of establishment of the steady potential.

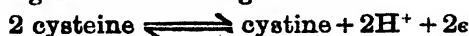
The values of the steady *E.M.F.* observed by us are somewhat different from the values of the electrode potential observed by Michaelis on a mercury surface exposed to a solution of cystine in absence of oxygen.

TABLE II

pH.	Mol. conc. of cystine.	Mol. conc. of cysteine.	$E.$	$E_0.$	$E_1-E_2^0$		
					Obs.	Calc. from (5)	Calc. from (6)
8.60 (1)	.0024	.0020	-.3458	.0800	.0557	.0556	0.0349
8.60 (2)	.0045	.0076	-.4015	.0803			
8.50 (1)	.0024	.0030	-.3510	.0801	.0104	.0111	.0078
8.50 (2)	.0018	.0040	-.3614	.0801			
8.40 (1)	.0024	.0018	-.3331	.0788	.0256	.0245	.0185
8.40 (2)	.0015	.0037	-.3587	.0784			
8.05 (1)	.0018	.0013	-.3060	.0906	.0322	.0316	.0223
8.05 (2)	.00087	.0031	-.3391	.0792			
7.5 (1)	.0034	.00084	-.2541	.0807	.0235	.0220	.0195
7.5 (2)	.0028	.0018	-.2776	.0792			

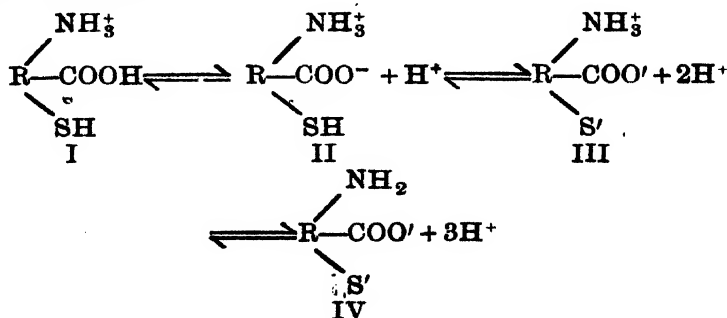
2.303 $RT/F = 0.059$ at 25° *Discussion.*

It will be seen from Table II that in neutral and in alkaline solutions the electrode potentials obtained at a mercury surface by the partial reduction of cystine *in situ* is due to a reversible transformation according to the following scheme.

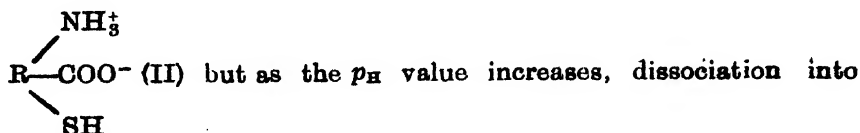


In acid solutions, however, the results are not capable of being expressed by any rational thermodynamic equation.

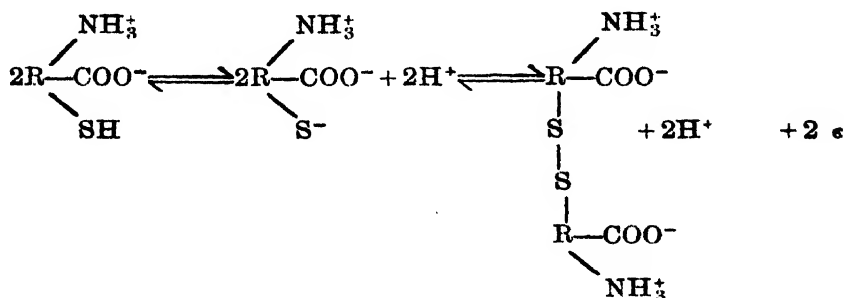
This behaviour can be correlated with the electrochemical and biochemical behaviour of cysteine and glutathione. Cannan and Knight (*Biochem. J.*, 1927, 21, 1389) consider that the cation of cysteine hydrochloride should be regarded as an acid dissociating three hydrogen ions thus:—



The respective dissociation constants are 1.4×10^{-2} , 7.8×10^{-9} , and 4.6×10^{-11} . Between p_H 3 and p_H 7 cysteine exists almost entirely as a neutral internal salt molecule



III and IV increases. Below p_H 7 the thiol groups (-SH) in cysteine (CSH) is stable but above this value the thiol group dissociates into $\text{S}^- + \text{H}^+$. It is in this region, when such dissociation becomes possible, that we should expect the thiol group to be an active reducing agent in a reversible transformation thus



The work of Hopkins (*Biochem. J.*, 1925, 19, 787) on the oxidation of fats and proteins by glutathione also brings out clearly the characteristic differences in the oxidation by thiol groups in acid and alkaline range. Thus in conformity with the investigations of Meyerhof (*Pflüger's Archiv*, 1923, 199, 531), Hopkins found that in acid range the oxidation of unsaturated fatty acids by oxygen of the air is catalytically accelerated by substances containing the thiol (SH) group. The thiol group forms with oxygen a peroxide $(\text{RSH})_2\text{O}_2$ which completely transfers the oxygen to the acceptor fatty acid resulting in regeneration of the thiol group. In alkaline range however, the (SH) group is so freely oxidisable that unless its concentration in the system be relatively high, it rapidly disappears even in the presence of fatty acids. In this region of p_H we are dealing with an induced reaction, the inductor, thiol compound and the acceptor fatty acid being both oxidised in the process. This difference in behaviour

can be explained by the hypothesis that in the formation of disulphide from two thiol molecules, the first stage consists in the dissociation of the thiol (SH) group into $\text{S}^- + \text{H}^+$. In the region of p_{H} where this dissociation is possible, oxidation of the thiol into the disulphide occurs. For the values of p_{H} below this range, a thiol compound is stable in the sense that it is incapable of forming a disulphide.

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Studies in Oxidation-Reduction Potential. Part II. Thioglycollic and Thiolactic Acids.

By J. C. GHOSH, S. N. RAYCHAUDHURI AND S. C. GANGULI.

In the preceeding paper, the oxidation-reduction potential of cystine and cysteine has been investigated in a solution at mercury cathode after forming the reductants *in situ* by the cathodic reduction of cystine in an atmosphere of pure nitrogen. The potential was shown to follow the thermodynamic equation

$$E = 0.0798 - \frac{RT}{F} p_H - \frac{RT}{F} \log \frac{[\text{cysteine}]}{\sqrt{[\text{cystine}]}}.$$

It was considered interesting to investigate the oxidation-reduction potentials of other sulphhydryl compounds, *e.g.* thioglycollic acid and thiolactic acid by the same method.

EXPERIMENTAL.

Two c.c. of a solution of thioglycollic acid or thiolactic acid exactly neutralised with caustic soda solution was oxidized by an exactly equivalent quantity of hydrogen peroxide and made up to 100 c.c. with buffer solution. This was then introduced within the electrolytic cell. The p_H value of the buffer solution was always determined electrometrically. Kahlbaum's thioglycollic acid was used.

Thiolactic acid was prepared from bromopropionic acid by potassium hydrosulphide by the method of Loven (*J. pr. Chem.*, 1884, **29**, 367). It was finally distilled at $100^\circ/15$ mm.

Measurements were made at a temperature of 30° . Experimental results above p_H 7 can be formulated by the thermodynamic equation

$$E = 0.0798 - \frac{RT}{F} p_H - \frac{RT}{F} \log \frac{[\text{reductant}]}{\sqrt{[\text{oxidant}]}} \quad \dots (1)$$

and also for the same p_H , the variation of *E.M.F.* with variation of the ratio of concentrations could be expressed by the equation

$$E_1 - E_2 = \frac{RT}{F} \log \frac{[\text{reductant}]_1 \cdot \sqrt{[\text{oxidant}]_2}}{\sqrt{[\text{oxidant}]_1} \cdot [\text{reductant}]_2} \quad (2)$$

Table I gives the potential at different p_H values and different concentrations of the oxidant and reductant.

TABLE I.

p_H	Mol. conc. oxidant.	Mol. conc. reductant.	E .	E_0 .	$E_1 - E_2$.	
					Obs.	Calc. from (2)
I. Thioglycollic acid.						
9.30 (i)	.0055	.011	-.4330	.0772	.0205	.0161
„ (ii)	.0079	.0071	-.4125	.0802		
8.55 (i)	.0046	.013	-.3916	.0791	.0232	.0229
„ (ii)	.0017	.019	-.4148	.0781		
7.00 (i)	.0079	.0065	-.2715	.0808	.0619	.0617
„ (ii)	.00037	.015	-.3334	.0805		
II. Thiolactic acid.						
9.35 (i)	.0050	.0032	-.4103	.0789	.0653	.0647
„ (ii)	.00049	.012	-.4756	.0803		
7.85 (i)	.0042	.0023	-.3116	.0795	.0318	.0318
„ (ii)	.0024	.0059	-.3434	.0800		

Discussion.

It is remarkable that the value of E_0 should be the same for thiolactic acid and thioglycollic acid as for cysteine. It is clear therefore that the reaction



has a value of free energy which is independent of the nature of the free radical to which the sulphur atom of the sulphhydryl group is attached.

It is interesting to note in this connection that the Raman spectra of all mercaptans and that of H_2S are identical, the shift being 2578 cm^{-1} . The same value of the Raman shift indicates that the force binding the hydrogen atom to the sulphur atom is always the same and independent of the way in which the other valency bonds of sulphur atom are saturated.

Behaviour of Nitrophenols with *p*-Toluenesulphonyl Chloride. Part II.

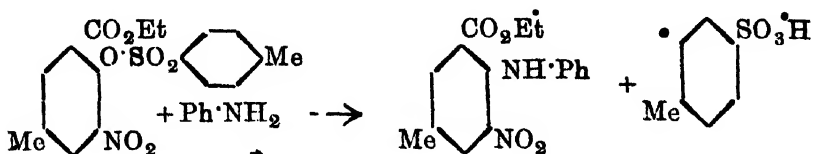
BY SHRIRANG M. SANE, SATYENDRA NATH CHAKRAVARTY
AND BIRENDRA NATH PARMANICK.

It was shown by one of us (Sane and Joshi, *J. Chem. Soc.*, 1924, 125, 2481) that OH group in nitrophenols, excepting 4-chloro-2: 6-dinitro-*m*-cresol* which gives ester, is replaced by chlorine by means of *p*-toluenesulphonyl chloride in presence of diethylaniline if there are two nitro groups present in *ortho* and *para* positions respectively to OH, but if sodium carbonate is used instead of diethylaniline, toluenesulphonyl ester is formed.

In the present paper this reaction has been extended to dinitrothymol, thymol, dinitrocarvacrol and nitro-*p*-cresotinic acid.* The first two like 4-chloro-2: 6-dinitro-*m*-cresols give *p*-toluenesulphonyl esters in presence of diethylaniline as well as sodium carbonate. The esters obtained are very stable and are not converted into diphenylamine derivatives when heated with aniline.

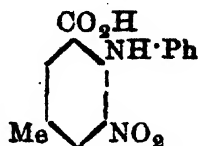
The nitro-*p*-cresotinic acid used in the experiment has probably nitro group in the *ortho* position to OH as during nitration of the cresotinic acid (Kostanecki and Niementoski, *Ber.*, 1885, 18, 254; Einhorn and Pfyl, *Annalen*, 1900, 311, 51), 2: 6-dinitro *p*-cresol (m. p. 82°) is formed, if the temperature is allowed to rise, the identity of which has been established by the preparation of the corresponding *p*-toluenesulphonyl ester, (m.p. 133°) (*cf.* Ullmann and Nadai, *Ber.*, 1908, 41, 1877).

The *p*-toluenesulphonyl compound of the ester of nitro-*p*-cresotinic acid is formed in presence of diethylaniline; it does not react with ammonia but unlike the corresponding compounds with dinitrocarvacrol and dinitrothymol, it gives diphenylamine derivative when boiled with aniline.



* Position 1 has been assigned to OH in cresols and hydroxy compounds and to COOH in cresotinic acids after the new edition of Beilstein (Vol. 6).

On hydrolysis this compound gives easily the free acid.



EXPERIMENTAL.

4:6-Dinitrothymol-*p*-toluenesulphonate.—A mixture of dinitrothymol (8 g.), *p*-toluenesulphonyl chloride (6.5 g.) and diethylaniline (15 c.c.) was heated on the water-bath for 4 hours. The cool mixture was then digested with dilute hydrochloric acid. The aqueous liquid was then decanted off and the liquid residue shaken with a little alcohol when it solidified. The ester dissolves easily in benzene and acetic acid, but is not easily soluble in alcohol. Colourless needles from acetic acid, m.p. 142°, yield 12 g. (Found: N, 7.02; S, 7.81. $C_{17}H_{18}O_7N_2S$ requires N, 7.1; S, 8.12 per cent.).

Dinitrothymol (4 g.) and *p*-toluenesulphonyl chloride (3.5 g.) were suspended in 20 c.c. of boiling water and sodium carbonate (3 g.) was added in small quantities at a time to the boiling mixture which was vigorously shaken during the reaction until the smell of *p*-toluenesulphonyl chloride disappeared. The cooled mixture was then filtered and the residue washed with sodium carbonate solution and recrystallised from alcohol, m.p. 142°. This ester is identical with the ester described above.

Dinitrocarvacrol-*p*-toluenesulphonate.—Dinitrocarvacrol (7 g.), *p*-toluenesulphonyl chloride (6.5 g.) and diethylaniline (15 c.c.) were heated together on the water-bath for 4 hours and the ester formed was obtained from it by the method already described. Colourless crystals from alcohol, m.p. 125°. The same ester is also obtained by using sodium carbonate as the condensing agent. (Found: N, 7.2; S, 8.23. $C_{17}H_{18}O_7N_2S$ requires N, 7.1; S, 8.12 per cent.).

Nitro-*p*-cresotinic acid.—Cresotinic acid (10 g.) was dissolved in acetic acid (80 c.c.) and nitric acid (6 c.c. *d* 1.4) dissolved in an equal quantity of acetic acid, was added to the solution. After a short time the colour changed and the mixture became warm. The nitro compound was then precipitated by the addition of ice to the mixture; m.p. 178°.

When the nitration was not controlled by cooling the mixture, carboxyl group was displaced and 2: 6-dinitro-*p*-cresol (m.p. 82°) was formed. The *p*-toluenesulphonate of the latter melted at 153°.

p-Toluenesulphonate of 2-hydroxy-3-nitro-5-methylbenzoic acid ethyl ester.—Nitro-*p*-cresotinic acid ethyl ester, (m.p. 104-105°, 2 g.), *p*-toluenesulphonyl chloride (2 g.) and diethylaniline (10 c.c.) were heated together on the water-bath and the toluenesulphonate separated as before. Colourless small plates from alcohol, m.p. 110°, yield 8 g. (Found: S, 8·27. $C_{17}H_{17}O_7NS$ requires S, 8·44 per cent.). Sodium carbonate was also used as condensing agent with the same result.

3-Methyl-5-nitro-6-diphenylamine benzoic acid ethyl ester.—*p*-Toluenesulphonate of nitrocresotinic acid ester (6 g.) and anhydrous sodium acetate (4 g.) were heated together with excess of aniline for some time. The excess of aniline was then removed by means of dilute HCl and the residue was crystallised from alcohol in yellowish needles, m. p. 136°. (Found: N, 9·26. $C_{16}H_{16}O_4N_2$ requires N, 9·83 per cent.).

3-Methyl-5-nitro-6-diphenylamine benzoic acid.—The foregoing compound was dissolved in alcohol and hydrolysed by HCl. Brick red small rhombic crystals from alcohol, m.p. 174°. (Found: C, 61·52; H, 4·88; N, 10·4. $C_{14}H_{12}O_4N_2$ requires C, 61·76; H, 4·41; N, 10·3 per cent.).

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Behaviour of Nitrophenols with *p*-Toluenesulphonyl Chloride. Part III.

By SHIRIRANG M. SANE AND SHIAM SUNDER JOSHI.

In the previous papers on this subject (*J. Chem. Soc.*, 1924, 125, 2481 ; *J. Indian Chem. Soc.*, 1932, 9,55) it was shown that when *p*-toluenesulphonyl chloride acts on nitrophenols in presence of diethylaniline, the OH group is replaced by Cl atom provided that nitro groups are present in the *ortho* and *para* positions with respect to OH group. It was also shown that the presence of a CH₃ group in the *meta* position with respect to OH acts unfavourably on the replaceability of the OH group. In the present paper we have examined the behaviour of the following phenol derivatives: 2-iodo-4:6-dinitrophenol; 2:6-dinitrophenol and its halogen derivatives viz., 4-bromo-2:6-dinitrophenol and 4-iodo-2:6-dinitrophenol; 3-chloro-2-bromo-4:6 dinitrophenol; 3-chloro-2-iodo-4:6-dinitrophenol; 3-chloro-2:4:6-trinitrophenol ; 3:6-dimethyl-2:4-dinitrophenol ; 2-hydroxy-4-methyl-5-nitrobenzoic acid ; 4-hydroxy-3-nitrobenzoic acid and 4-hydroxy-5-bromo-3-nitrobenzoic acid.

The results obtained are given in Table I. The chloro compounds formed contain an active chlorine atom and are capable of undergoing various reactions. These will be described in a later paper. Some of the *p*-toluenesulphonic acid esters are also more or less reactive, while the others are not.

Acetyl and benzoyl derivatives of some phenols used have been described in the experimental part.

EXPERIMENTAL.

2-Iodo-4:6-dinitrophenyl-*p*-toluenesulphonate.—2-Iodo-4:6-dinitrophenol (3.1 g.) and *p*-toluenesulphonyl chloride (2.1 g.) were boiled together with water and to the hot mass sodium carbonate (1.2 g.) was added in small quantities and the liquid well shaken. The mixture was then allowed to cool and then filtered. The ester (3 g.) dissolved easily in benzene and with difficulty in alcohol from which it crystallises in colourless crystals, m.p. 149°. (Found: S, 6.71. C₁₃H₉O₇N₂IS requires S, 6.9 per cent.).

1-Chloro-2-iodo-4-(3-dinitrobenzene).—A mixture of 2-iodo-4:6-dinitrophenol (8 g.), *p*-toluenesulphonyl chloride (4.1 g.) and diethylaniline (12 c.c.) was heated on the water-bath for four hours. From the dark product the diethylaniline was removed by dilute hydrochloric acid and the unchanged phenol by sodium carbonate solution. The crude product (4.5 g.) was dissolved in alcohol and the solution boiled with animal charcoal. From the filtered and concentrated solution, the chloriododinitrobenzene separated out in pale white crystals, m.p. 106°. It dissolves in all the common organic solvents. (Found : N, 8.61. $C_6H_2O_4N_2Cl$ I requires N, 8.53 per cent.).

2:6-Dinitrophenyl-*p*-toluenesulphonate.—This ester was obtained from 2:6-dinitrophenol (4.6 g.), *p*-toluenesulphonyl chloride (5.2 g.) and sodium carbonate (8 g.) in the manner already described. It dissolves easily in benzene and acetone and with difficulty in alcohol. Colourless crystals from a mixture of alcohol and acetone, m.p. 135°, yield 6 g. (Found : S, 9.15. $C_{13}H_{10}O_7N_2S$ requires S, 9.47 per cent.).

1-Chloro-2:6-dinitrobenzene.—This is obtained from 2:6-dinitrophenol (4.6 g.), *p*-toluenesulphonyl chloride (5.2 g.) and diethylaniline (9 c.c.) in the manner already described. It forms colourless crystals, m.p. 86°, yield 3 g. It dissolves easily in alcohol, benzene, etc. This is identical with the chlorodinitrobenzene prepared by Ostromisslenski (*J. pr. Chem.*, 1908, ii, 78, 261). (Found : N, 13.56 ; Cl, 17.43. $C_6H_3O_4N_2Cl$ requires N, 13.88 ; Cl, 17.53 per cent.).

4-Bromo-2:6-Dinitrophenyl-*p*-toluenesulphonate.—This was obtained from *p*-toluenesulphonyl chloride (4.2 g.), sodium carbonate (2.5 g.) and 4-bromo-2:6-dinitrophenol (5.3 g.). The last compound was obtained from 2:6-dinitrophenol by adding the required amount of bromine to its solution in alcohol (Fromm and Ebert, *J. pr. Chem.*, 1922, ii, 106, 75). The ester, forms colourless crystals, melts at 136°, yield 6 g. (Found : S, 7.84. $C_{13}H_9O_7N_2BrS$ requires S, 7.67 per cent.).

1-Chloro-2:6-dinitro-4-bromobenzene.—This was obtained from 4-bromo-2:6-dinitrophenol (8 g.), *p*-toluenesulphonyl chloride (6.4 g.) and diethylaniline (16 c.c.). It is soluble in most of the organic solvents and is obtained as pale white crystals from dilute acetic acid, m.p. 98°, yield 4.8 g. (Found : N, 10.17 ; Cl + Br, 40.74. $C_6H_2O_4N_2ClBr$ requires N, 9.95 ; Cl + Br, 41.03 per cent.).

4-Iodo-2:6-dinitrophenyl-*p*-toluenesulphonate.—This was prepared from 4-iodo-2:6-dinitrophenol (3.1 g.) (Armstrong, *loc. cit.*),

p-toluenesulphonyl chloride (2.1 g.) and sodium carbonate (1.3 g.). Colourless crystals from a mixture of acetone and alcohol, m.p. 138°, yield 4 g. (Found: S, 6.95. $C_{13}H_9O_7N_2S$ requires S, 6.9 per cent.).

1-Chloro-4-iodo-2:6-dinitrobenzene.—This was obtained from 4-iodo-2:6-dinitrophenol (10.5 g.), *p*-toluenesulphonyl chloride (7 g.) and diethylaniline (22 c.c.). It is soluble in most organic solvents; colourless crystals from alcohol, m.p. 115°, yield 6 g. (Found: N, 8.86. $C_6H_2O_4N_2ClI$ requires N, 8.53 per cent.).

3-Chloro-2-bromo-4:6-dinitrophenol.—To a solution of 3-chloro-4:6-dinitrophenol (6.5 g.) in alcohol, bromine (1.6 c.c.) was added drop by drop. The reaction product was warmed and then poured on ice when chlorobromodinitrophenol (8.3 g.) separated out. It dissolves in most organic solvents and crystallises from methyl alcohol in colourless crystals, m.p. 118°. (Found: N, 9.16. $C_6H_3O_5N_2ClBr$ requires N, 9.41 per cent.).

3-Chloro-2-bromo-4:6-dinitrophenyl-*p*-toluenesulphonate, obtained from 3-chloro-2-bromo-4:6-dinitrophenol (3 g.), *p*-toluenesulphonyl chloride (2.1 g.) and sodium carbonate (1.2 g.), is easily soluble in benzene. Colourless crystals from acetone-alcohol mixture; m.p. 125°, yield 2 g. (Found: S, 7.01. $C_{13}H_8O_7N_2ClBrS$ requires S, 7.08 per cent.).

1:3-Dichloro-2-bromo-4:6-dinitrobenzene.—This was prepared from 3-chloro-2-bromo-4:6-dinitrophenol (6 g.), *p*-toluenesulphonyl chloride (4.2 g.) and diethylaniline (12 c.c.). Dichlorobromodinitrobenzene dissolves easily in most organic solvents; colourless crystals, m.p. 108°, yield 5 g. (Found: N, 9.18. $C_6HO_4N_2Cl_2Br$ requires N, 8.86 per cent.).

3-Chloro-2-iodo-4:6-dinitrophenol.—The compound was prepared by adding iodine (7.6 g.) and mercuric oxide alternately to 3-chloro-4:6-dinitrophenol (6.4 g.) in alcohol. The alcohol was then distilled off and the residue repeatedly extracted with benzene. Chloriodo-dinitrophenol forms yellow crystals, m.p. 108°, yield 9.5 g. It dissolves in most organic solvents. (Found: N, 7.81. $C_6H_3O_5N_2ClI$ requires N, 8.13 per cent.).

3-Chloro-2-iodo-4:6-dinitrophenyltoluenesulphonate.—This was obtained from 3-chloro-2-iodo-4:6-dinitrophenol (3.5 g.), *p*-toluenesulphonyl chloride (2.1 g.) and sodium carbonate (1.2 g.). The ester forms colourless crystals, m.p. 150°, yield 3 g. (Found: S, 6.27. $C_{13}H_8O_7N_2ClI$ requires S, 6.43 per cent.).

1:3-Dichloro-2-iodo-4:6-dinitrobenzene.—This was prepared from a mixture of 3-chloro-2-iodo-4:6-dinitrophenol (3.5 g.), *p*-toluenesulphonyl chloride (2.1 g.) and diethylaniline (7 c.c.). Dichloriodo-dinitrobenzene is soluble in most organic solvents. Pale white crystals, m.p. 108°, yield 2 g. (Found: N, 7.99. $C_6H_2O_4N_2Cl_2I$ requires N, 7.7 per cent.).

1:3-Dichloro-2:4:6-trinitrobenzene.—This was prepared from a mixture of 3-chloro-2:4:6-trinitrophenol (8 g.) (obtained by nitrating *m*-chlorophenol; cf. Tijmstra *Chem. Zentr.*, 1902, II, 519), *p*-toluenesulphonyl chloride (6.8) and diethylaniline (15 c.c.). Colourless crystals, m.p. 129°, yield 6 g. (Sudborough and Picton, *J. Chem. Soc.*, 1906, 89, 591). (Found: N, 14.63. $C_6H_2O_6N_3Cl_2$ requires N, 14.89 per cent.).

3:6-dimethyl-2:4-dinitrophenyl-*p*-toluenesulphonate was prepared from 3:6-dimethyl-2:4-dinitrophenol (2.1 g.) (Kostanocki, *Ber.*, 1886, 19, 2321), *p*-toluenesulphonyl chloride (2.1 g.) and diethylaniline (15 c.c.). The ester crystallises from acetone-alcohol mixture in colourless crystals, m.p. 137°, yield 3.2 g. (Found: S, 8.97. $C_{15}H_{14}O_7N_2S$ requires S, 8.74 per cent.).

2-Hydroxy-4-methyl-5-nitromethylbenzoate.—2-Hydroxy-4-methyl-5-nitrobenzoic acid (5 g.), which was prepared by nitrating 2-hydroxy-4-methylbenzoic acid (Borsche, *Annalen*, 1904 330, 1000) was dissolved in methyl alcohol (20 c.c.) and concentrated sulphuric acid (2 c.c.) added to the mixture. The mixture was boiled for three hours, the excess of methyl alcohol distilled off and the residue diluted with ice cold water. The ester crystallises from methyl alcohol in colourless crystals, m.p. 78°, yield 4.5 g. (Found: N, 6.53. $C_9H_9O_5N$ requires N, 6.68 per cent.).

***p*-Toluenesulphonic ester of 2-hydroxy-4-methyl-5-nitromethylbenzoate** was obtained from the foregoing methylbenzoate (4.2 g.), *p*-toluenesulphonyl chloride (4.2 g.), and diethylaniline (9 c.c.). The ester forms colourless crystals, m.p. 93°, yield 6 g. (Found: S, 8.91. $C_{16}H_{15}O_7NS$ requires S, 8.77 per cent.).

2-Phenylamine-4-methyl-5-nitromethylbenzoate.—The foregoing ester (2 g.) and aniline (4 c.c.) were boiled together for a few minutes. On dissolving out the excess of aniline by hydrochloric acid, the phenylaminomethylnitromethylbenzoate separated out. This compound dissolves easily in the common organic solvents and crystallises from alcohol in yellow crystals, m.p. 84°, yield 1.3 g. (Found: N, 9.45. $C_{15}H_{14}O_4N_2$ requires N, 9.79 per cent.).

p-Toluenesulphonic ester of 4-hydroxy-3-nitromethylbenzoate — 4-Hydroxy-3-nitromethylbenzoate (4 g.) (Auwers and Rohrig, *Ber.*, 1897, 30, 991; D.R.P. 97334), *p*-toluenesulphonyl chloride (4.2 g.) and diethylaniline (8 c.c.) were heated together on the water-bath. The ester is obtained in colourless crystals from alcohol, m.p. 86°, yield 6 g. (Found: S, 9.17. $C_{15}H_{13}O_7NS$ requires S, 9.12 per cent.).

4-Phenylamino-3-nitromethylbenzoate.—*p*-Toluenesulphonic ester of 4-hydroxy-3-nitromethylbenzoate (3.5 g.) and aniline (5 c.c.) were heated together for some time. On removing the excess of aniline by hydrochloric acid, the reaction product separated out. Shining yellow crystals from alcohol, m.p. 127°, yield 2.3 g. (Found: N, 10.46. $C_{14}H_{12}O_4N_2$ requires N, 10.30 per cent.).

4-Hydroxy-5-bromo-3-nitrobenzoic acid.—This was prepared by adding bromine (2.7 c.c.) to a solution of 4-hydroxy-3-nitrobenzoic acid (9 g.) (*Ber.*, 1887, 20, 408; *J. pr. Chem.*, 1890, ii, 42, 552), in acetic acid (20 c.c.). On adding water to the product of reaction the hydroxybromonitrobenzoic acid separated out (11 g.). It dissolves easily in the common organic solvents; colourless crystals from dilute acetic acid, m.p. 229°. (Found: N, 5.28. $C_7H_4O_5NBr$ requires N, 5.34 per cent.). The methyl ester of the foregoing compound melts at 130°. (Found: N, 5.09. $C_8H_6O_5NBr$ requires N, 5.07 per cent.).

p-Toluenesulphonic ester of 4-hydroxy-3-nitro-5-bromomethylbenzoate.—This was obtained from 4-hydroxy-3-nitro-5-bromomethylbenzoate (2.8 g.), *p*-toluenesulphonyl chloride (2.1 g.) and diethylaniline (5 c.c.). The ester dissolves easily in most organic solvents; colourless crystals, m.p. 127°, yield 3.6 g. (Found: S, 7.41. $C_{15}H_{12}O_7NBrS$ requires S, 7.44 per cent.).

4-Phenylamino-3-nitro-5-bromomethylbenzoate.—The foregoing ester (2.2 g.) and aniline (5 c.c.) were heated together for sometime. On removing the excess of aniline, the phenylamine derivative separates out (1.5 g.). Deep yellow shining crystals from alcohol, m.p. 128°. (Found: N, 8.06. $C_{14}H_{11}O_4N_2Br$ requires N, 7.98 per cent.).

Acetyl derivative of 2-iodo-4:6-dinitrophenol was obtained in shining colourless crystals from alcohol, m.p. 113°. (Found: N, 7.68. $C_8H_5O_6N_2I$ requires N, 7.96 per cent.).

Benzoyl derivative of 2-bromo-4:6-dinitrophenol formed colourless crystals from dilute alcohol, m.p. 94°. (Found: N, 7.39. $C_{13}H_7O_6N_2Br$ requires N, 7.63 per cent.).

Benzoyl derivative of 4-iodo-2:6-dinitrophenol was obtained in colourless crystals from alcohol, m.p. 175°. (Found: N, 6.98. $C_{13}H_7O_6N_2I$ requires N, 6.76 per cent.).

Acetyl derivative of 3:6-dimethyl-2:4-dinitrophenol formed colourless crystals from alcohol, m.p. 102°. (Found: N, 10.89. $C_{10}H_{10}O_6N_2$ requires N, 11.02 per cent.).

Benzoyl derivative gave colourless crystals from alcohol, m.p. 124°. (Found: N, 8.63. $C_{15}H_{12}O_6N_2$ requires N, 8.86 per cent.).

*Benzoyl derivative of 4:6-dinitro-*m*-cresol (OH=1, CH₃=3)*: gave colourless crystals from alcohol, m.p. 95°. (Found: N, 9.19. $C_{14}H_{10}O_6N_2$ requires N, 9.27 per cent.).

*Acetyl derivative of 2-chloro-4:6-dinitro-*m*-cresol (OH=1, CH₃=3)* gave colourless crystals from alcohol, m.p. 118°. (Found: N, 10.46. $C_9H_7O_6N_2Cl$ requires N, 10.2 per cent.).

*Benzoyl derivative of 2-chloro-4:6-dinitro-*m*-cresol (OH=1, CH₃=3)* gave colourless crystal from alcohol, m.p. 117°. (Found: N, 8.13. $C_{14}H_9O_6N_2Cl$ requires N, 8.32 per cent.).

TABLE I.

Phenols.	Product of reaction with <i>p</i> -toluenesulphonyl chloride.		Ester-reactive or not.
	Ester.	Chloro- compound.	
*1. 2:4:6-Tribromophenol	Formed.	...	Not reactive
*2. 2:4-Dibromo-6-nitrophenol	„	...	„
*3. 2:6-Dibromo-4-nitrophenol	„	...	„
†4. 2:6-Dinitro- <i>m</i> -cresol (OH=1)	„	...	Reactive
†5. 2-Bromo-4:6-dinitro- <i>m</i> -cresol (OH=1)	„	Formed	„
*6. 4-Chloro-2:6-dinitro- <i>m</i> -cresol (OH=1)	„	...	Not reactive
7. 3:6-Dimethyl-2:4-dinitro- phenol	„	...	„
*8. 2-Bromo-4:6-dinitrophenol	„	Formed	Reactive
9. 2-Iodo-4:6-dinitrophenol	„	„	„

* *cf.* J. Chem. Soc., 1924, 125, 2482.

† *cf.* J. Indian Chem. Soc., 1928, 5, 800.

TABLE I—*contd.*

Phenols.	Product of reaction with <i>p</i> -toluenesulphonyl chloride.		Ester-reactive or not.
	Ester.	Chloro- compound.	
10. 2:6 :dinitrophenol	Formed.	Formed	Reactive
11. 4-Bromo-2 :6-dinitrophenol	„	„	„
12. 4-Iodo-2 :6-dinitrophenol	„	„	„
13. 3-Chloro-4 :6-dinitrophenol	„	„	„
14. 3-Chloro-2-bromo 4 :6-dinitro- phenol	„	„	„
15. 3-Chloro-2-iodo-4 :6-dinitro- phenol	„	„	„
16. 3-Chloro-2 :4 : 6-trinitrophenol	Not formed	„	...
17. 2-Hydroxy-4-methyl-5-nitro- methylbenzoate	Formed	...	Partly reactive
18. 4-Hydroxy-3-nitromethylben- zoate	„	...	„ „
19. 4-Hydroxy-5-bromo-3-nitro- methylbenzoate	„	...	„ „
†20. Dinitrothymol	„	...	Not reactive
†21. Dinitrocarvacrol	„	...	„
†22. 2-Hydroxy-3-nitro-5-methyl- ethylbenzoate	„	...	Partly reactive

We are indebted to Messrs Meister Lucius and Brunning, Höchst a/m (Germany), who generously placed a sufficient quantity of 2:6-dinitrophenol at our disposal.

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LUCKNOW UNIVERSITY.

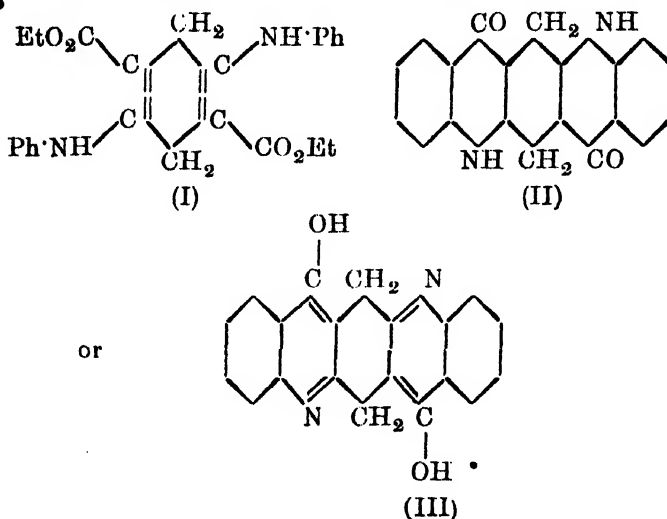
Received May 12, 1930. •

Hetero-ring Formation from Anilino Derivatives of Succinosuccinic Ester.

By GAJANAN PURUSHOTTAM PENDSE AND SIKHIBHUSHAN DUTT.

Libermann (*Annalen*, 1914, **404**, 272) condensed methyl succinosuccinate with ammonia, which yielded a coloured substance, dimethyl-2:5-diamino- Δ^1 :4-cyclohexadiene-1:4-dicarboxylate. He also condensed various aromatic primary amines with succinosuccinic ester and obtained corresponding products, which on oxidation with iodine yielded corresponding terephthalates. The above work was subsequently supplemented by Migliacci and Gargiulo (*Gazzetta*, 1927, **57**, 914; 1928, **58**, 110).

The internal condensation of diarylamino condensation products of ethyl succinosuccinate (I) with formation of pyridine derivatives (II) has now been brought about by the action of alcoholic sodium ethoxide, and in many cases even by the action of concentrated aqueous sodium hydroxide solution; the resultant



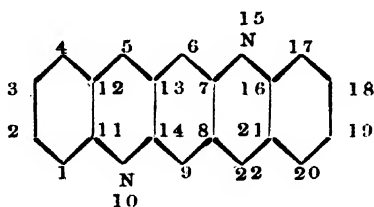
pyridine derivatives can be represented by (II) or (III) on account of the possibility of keto-enol type of tautomerism which is borne out by experimental facts. →

Compounds of this type are invariably coloured in the solid state (crimson, violet or blue) and dissolve to a yellow solution in caustic alkalis, the original compound being reprecipitated unchanged by

dilute acids. This remarkable change of colour on the addition of alkali is probably due to the keto-enol change. These compounds dissolve in concentrated sulphuric acid yielding intensely coloured (blue or green) solutions from which the original compounds are re-precipitated on dilution with water. All the compounds described in this paper are intensely coloured substances ranging from pink or crimson to blue or green in shade. They dye wool or silk from an acid bath containing the dyestuff in fine suspension to beautiful shades; they do not however dye cotton. The absorption maxima of these compounds have been determined in the experimental.

The facts that the compounds dissolve in concentrated sulphuric acid with deep blue or green colour and also that they do not liberate carbon dioxide on the addition of dilute sodium bicarbonate and do not yield metallic salts or esters, show clearly enough that they are entirely different from the diarylaminoterephthalic acids prepared by Libermann (*loc. cit.*).

The nomenclature of these compounds have been based on the consideration that they may be supposed to be derivatives of acridinolines (like acridindoles of Clemo, Perkin and Robinson, *J. Chem. Soc.*, 1924, 125, 1769) of the following skeleton:



The following aromatic primary amines have been condensed with ethyl succinosuccinate and the condensation products subsequently treated with alcoholic sodium ethoxide for internal condensation and formation of the corresponding hetero-ring compound: aniline, *o*-, *m*- and *p*-toluidines, *o*- and *p*-anisidines, *o*- and *p*-phenetidines, 1:3:4-xylidine, α - and β -naphthylamines, *o*- and *p*-aminophenols, *o*-aminoacetanilide and *p*-aminoacetophenone. Attempts to prepare heteroring compounds from primary diamines and secondary amines were unsuccessful.

EXPERIMENTAL.

The condensation of ethyl succinosuccinate with primary aromatic amines were carried out with only slight modifications of the original method described by Libermann (*loc. cit.*) to suit individual

cases. The properties of these compounds, many of which have now been prepared for the first time, have been given in Table I.

The above mentioned anilino derivatives of succinosuccinic esters were then subjected to internal condensation to yield the final hetero-ring compounds. The preparation of one of them is given below. The rest were prepared in similar ways with slight modification according to individual cases.

6: 9-Dihydro-5: 22-dihydroxyacriquinoline.

2: 5-Dianilinocyclohexane-1: 4-dicarboxylate (3 g.) was refluxed for about three hours with a freshly prepared solution of sodium ethoxide (30 c.c. of 10 p.c.) in absolute alcohol. The colour of the solution gradually changed from dark orange to light yellow as the reaction proceeded to completion and the disodium salt of the condensation product was deposited in crystalline flakes at the bottom of the reaction vessel. The mixture was then cooled, diluted with water, filtered and the yellow filtrate acidified with dilute hydrochloric acid when a fine violet precipitate was thrown down. This was collected and crystallised from dilute alcohol.

Generally speaking all these types of compounds are soluble in alcohol, acetone, acetic acid and pyridine etc., but insoluble in benzene or ether. The properties of these compounds are summarised in Table II.

TABLE I.

Condensation Products of Succinosuccinic Ester with Primary Aromatic Amines.

(-cycloHexane-1:4:-dicarboxylate=C).

Name.	M. p.	Appearance.
Diethyl-2:5-dianilino-C.	163°	Orange red needles.
Diethyl-2:5-di-o-toluidino-C.	181°	Orange to deep rose red needles.*
*Diethyl-2:5-di-m-toluidino-C.	143°	Yellowish red needles.
Diethyl-2:5-di-p-toluidino-C.	214°	Deep orange red needles.
Diethyl-2:5-di-o-anisidino-C.	159°	Scarlet red prisms.
Diethyl-2:5-di-p-anisidino-C.	191°	Orange needles.
Diethyl-2:5-di-o-phenatidino-C.	201°	Scarlet red needles.
Diethyl-2:5-di-p-phenatidino-C.	197°	Deep red crystals.*
*Diethyl-2:5-di-l-xylylidino-C.	155°	Orange red needles.
Diethyl-2:5-di-α-naphthylamino-C.	230°	" " "
Diethyl-2:5-di-β-naphthylamino-C.	228°	Rose needles.
*Diethyl-2:5-di-o-hydroxyamino-C.	122°	Deep red needles.
*Diethyl-2:5-di-p-acetylaminoanilino-C.	113°	Reddish brown crystals.
*Diethyl-2:5-di-p-acetylaminoanilino-C.	179°	" " "
*Diethyl-2:5-di-p-acetylanilino-C.	119°	" " "

* New compounds prepared by the authors.

TABLE II.
Hetero-ring Compounds.

(6:9-Dihydro-5:22-dihydroxyacriquinoline=Q).

Name.	Appearance.	Shade on wool and silk.	Wave-length of absorption maxima.	M. p.	Analysis Found.	(nitrogen). Calc.
Q.						
1:17-Dimethyl-Q.	Violet prisms.	Deep pink.	4520	Above	8.78	9.9 p.c.
2:18-Dimethyl-Q.	Bluish violet prisms.	Light red.	4870	Decomposed at 255°	8.42	8.18
3:19-Dimethyl-Q.	" needles	Pinkish violet.	4590	258°	7.7	8.18
1:17-Dimethyl-Q.	Pinkish violet crystals.	" "	4890	212°	8.3	8.18
1:17-Dimethoxy-Q.	Violet needles.	" "	4370	Above	7.7	7.48
3:19-Dimethoxy-Q.	Deep violet crystals.	Bright red.	4960	"	7.9	7.48
1:17-Dimethoxy-Q.	Pinkish violet prisms.	Deep yellow.	4490	"	6.6	6.96
1:17-Diethoxy-Q.	" "	Pink.	5170	218°	7.0	6.96
3:19-Diethoxy-Q.	Deep violet needles.	"	4460	Above	7.4	7.57
1:17:8:19-Tetramethyl-Q.	" crystals.	"	4980	"	6.93	6.76
1:2:17:18-Diphenylene-Q.	" prisms.	Light red.	5250	"	7.12	6.76
3:4:19:20-Diphenylene-Q.	Deep reddish brown crystals.	Brownish yellow.	4210	236°	7.6	8.08
1:17-Dihydroxy-Q.	Pinkish violet prisms.	Deep pink.	4710	205°	8.1	8.08
3:19-Dihydroxy-Q.	" brown crystals.	Yellowish red.	4990	212°	12.7	13.08
3:19-Diacetyldiamino-Q.	Yellow needles.	Yellowish brown.	4330	158°	7.2	7.04

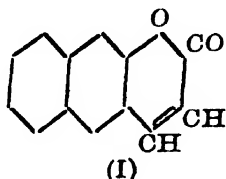
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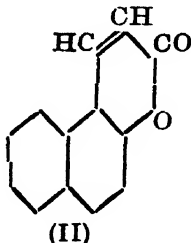
Constitution of β -Naphthapyrones.

By BIMAN BIHARI DEY, RUBUGUNDAY HARI RAMACHANDRA RAU AND
YEGNARAMA SANKARANARAYANAN.

There has been considerable uncertainty regarding the structures of the coumarins derived from β -naphthol. Kauffmann (*Ber.*, 1883, 16, 683), who obtained a naphthapyrone (m.p. 118°) by heating β -naphthol-aldehyde with sodium acetate and acetic anhydride, formulated it as 1:2- $\beta\beta$ -naphthapyrone having the constitution (I).



It will be readily seen, however, that since the aldehyde group in β -naphthol-aldehyde may be attached to either position 1 or position 3 in the naphthalene ring, the pyrone derived from it may have the following alternative structure of 1:2- $\beta\alpha$ -naphthapyrone (II).



Kauffmann himself regarded his aldehyde (m.p. 81°) as β -naphthol- β -aldehyde, and hence assigned formula (I) to his pyrone. Gattermann (*Ber.*, 1899, 32, 285), on the other hand, in view of the great mobility of the α -hydrogen atom in β -naphthol, formulated the same aldehyde as β -naphthol- α -aldehyde. In the latter case, the pyrone derived from it would obviously have formula (II).

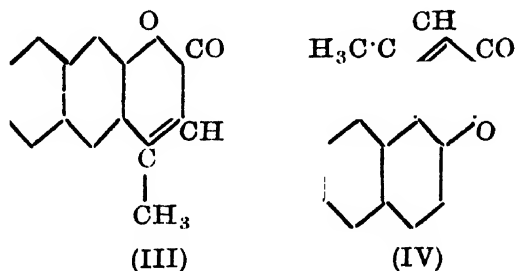
Pechmann and Welsh (*Ber.*, 1884, 17, 1651) claimed to have prepared, by the usual method of condensation of β -naphthol and malic acid in presence of hot concentrated sulphuric acid, a β -naphthapyrone crystallising in yellow needles (m.p. 141°), different from that described by Kauffmann, but no definite structure seems to

have been assigned to the compound by these authors. Since then, it has been customary in literature to refer to Kauffmann's compound as β -naphthacoumarin and to Pechmann's compound as *iso*- β -naphthacoumarin, without defining clearly the precise nature of their difference.

The aldehyde prepared from β -naphthol in the usual manner is now generally considered to be the 2-hydroxy-1-naphthaldehyde, but direct proof of such a constitution has been lacking. Recently, however, Boehm and Profft (*Arch. Pharm.*, 1931, **269**, 25, 37) claim to have synthesised the isomeric 2-hydroxy-3-naphthaldehyde (m.p. 99-100°) by the reduction of the acid chloride of 2-naphthol-3-carboxylic acid with palladised barium sulphate, thereby setting at rest all doubts regarding the constitution of the other aldehyde. Boehm and Profft have also succeeded in preparing from the new aldehyde, by the application of Perkin's reaction, another isomeric β -naphthacoumarin (m.p. 164°) which is different from both Kauffmann's and Pechmann's compounds, and which must obviously be the 1:2- $\beta\beta$ -naphthapyrone of structure (I). The formulæ of the two β -naphthacoumarins prepared by Kauffmann (structure II) and by Boehm and Profft (structure I) respectively, having thus been definitely established, there remains no other suitable alternative formula to be ascribed to the compound (m.p. 141°) described by Pechmann and Welsh (*loc. cit.*). Moreover, the melting point recorded for the latter compound is found to be the same as that of α -naphthacoumarin (1:2- $\alpha\beta$ -naphthapyrone), and it seemed, therefore, to be very necessary to clear up all doubts or confusion existing in the matter by a careful repetition of Pechmann and Welsh's work. The condensation of β -naphthol and malic acid has now been carried out several times with all necessary precautions; the results, which are the same in all cases, are found to be very different from those recorded by previous workers. An orange yellow substance with a beautiful green metallic reflex and of a highly colloidal character, not melting even at 320°, was invariably obtained, while the aqueous sulphuric acid solution yielded, on repeated extraction with ether, a small amount of colourless crystals (m.p. 118°) which was identified as Kauffmann's β -naphthacoumarin, both by analysis and by the method of mixed melting points. No trace of the compound (m.p. 141°) mentioned by Pechmann and Welsh (*loc. cit.*) was ever obtained. The orange solid, which is soluble to some extent in water, appears to have an acidic character as it dissolves in cold alkalis and even in

alkali carbonates to form perfectly colourless solutions. Indeed, the change from deep orange to colourless is so sharp and marked that the substance ought to serve as an excellent indicator for alkalis. Acids reprecipitate the orange solid in a finely divided, almost colloidal condition. This interesting body has so far been obtained in only very poor yields, and a fuller account of its composition and properties has to be deferred till a sufficient quantity has been accumulated.

The problem of the constitution of the methyl- β -naphthacoumarin obtained from β -naphthol and ethyl acetoacetate (Bacovescu, *Ber.*, 1910, 43, 1280) has also not been satisfactorily solved. Two alternative structures, corresponding to (I) or (II), are also possible in this case, according as the carbon atom in the naphthalene nucleus taking part in this condensation is in 1 or 3 positions, thus:—

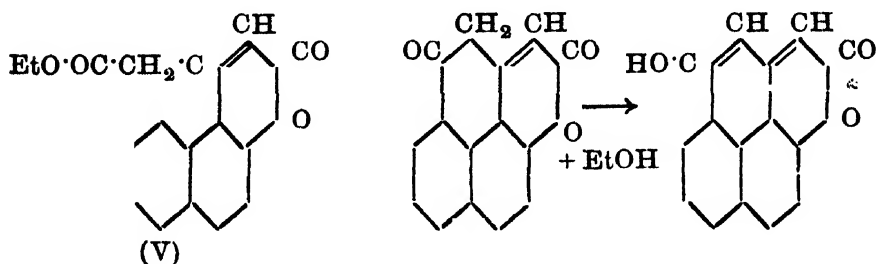


Attempts were made (Dey, *J. Chem. Soc.*, 1915, 107, 1615) to arrive at a choice between these two constitutions by oxidising the 4-methyl- β -naphthapyrone to the corresponding 2:3-(or 1:1)-naphthol-carboxylic acid, but they have hitherto been unsuccessful. The structure (IV) has however been advocated for this coumarin, although no direct proof of this constitution is available, mainly on the following grounds:

(a) The condensations of phenols with malic acid, and with ethyl acetoacetate, in presence of sulphuric acid, have always been found to proceed on the same lines, the unsubstituted coumarins and the corresponding 4-methyl substituted coumarins being respectively obtained by the two reactions.

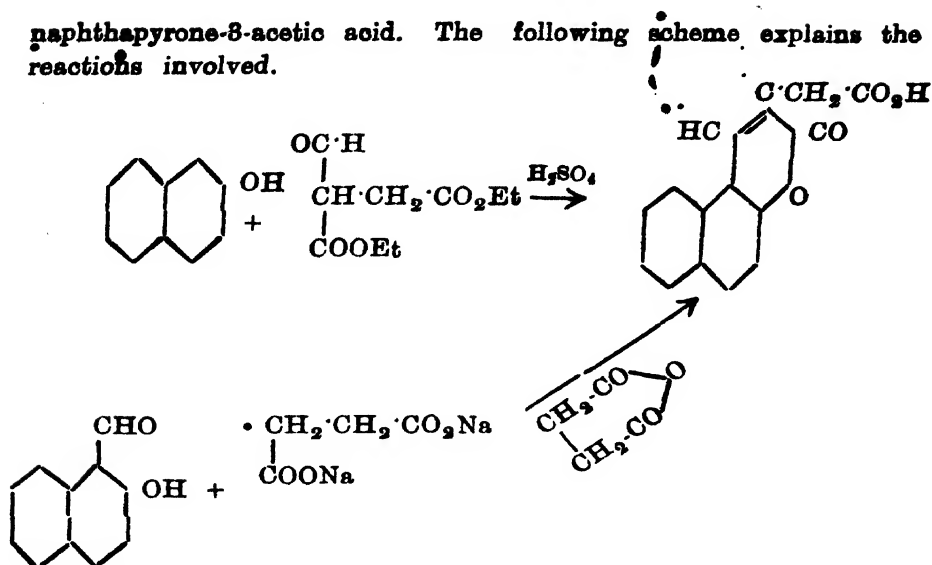
(b) Since it is now definitely proved that the product of condensation of β -naphthol and malic acid is identical with the coumarin obtained by Kauffmann from 2-hydroxy-1-naphthaldehyde, and has, therefore, structure (II), it may reasonably be inferred that the methyl-naphthacoumarin prepared from β -naphthol and ethyl acetoacetate has also a similar, i.e., β -structure (IV).

(c) An additional and important reason for giving preference to structure (IV) lay in the observation (Dey, *loc. cit.*, 1916) that the ethyl ester of the naphthacoumarin-4-acetic acid prepared from β -naphthol and ethylacetone dicarboxylate, behave differently from the other coumarin-4-acetic acid ethyl esters and also from the isomeric α -naphthacoumarin-4-acetic acid ethyl ester prepared from α -naphthol and ethylacetone dicarboxylate, the latter being known to have structures akin to (III). On warming the ester with concentrated sulphuric acid, it lost the elements of a molecule of alcohol and formed a compound of the formula $C_{15}H_8O_3$. Since this reaction is exceptional, the other coumarin-4-acetic acids remaining unchanged under these conditions, it has been interpreted as evidence in favour of structure (IV) for β -naphthacoumarin-4-acetic acid, and therefore for 4-methyl- β -naphthacoumarin, the latter being obtained quantitatively from the former by heating above its melting point. The compound, $C_{15}H_8O_3$ designated 5-hydroxy-2-keto-peri-peri-naphthindenofuran, is supposed to be formed in the following manner:—



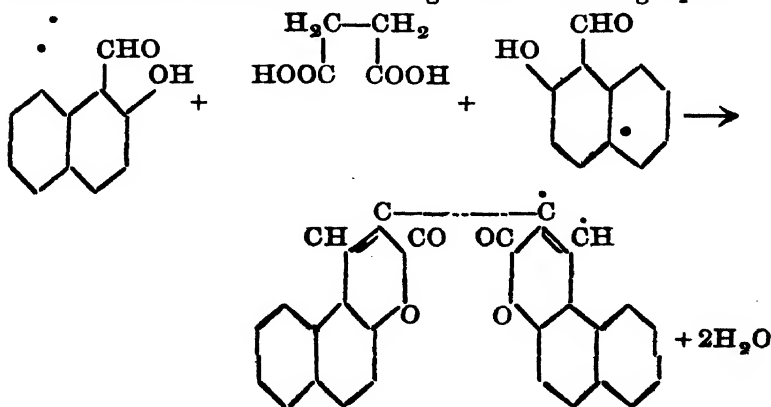
If this interpretation be accepted it would undoubtedly constitute an important evidence in favour of structures (IV) and (V) for methyl- β -naphthacoumarin and β -naphthacoumarin-4-acetic acid respectively. It must nevertheless be recognised that the arguments which have so far been adduced seem to furnish only indirect proofs, and fresh and more direct evidence in support of the proposed constitutions would be most welcome. This has now been obtained in connection with the study of coumarin-3-acetic acids which has been recently started in this laboratory. β -Naphthol is found to condense with ethylformyl succinate in presence of sulphuric acid in the normal manner giving rise to a coumarin-3-acetic acid, m.p. 264° , (methyl ester, m.p. 149°) (Dey and Sankaranarayanan, *J. Indian Chem. Soc.*, 1931, 8, 827). The same acid has now been synthesised from 2-hydroxy-1-naphthaldehyde by heating with sodium succinate and succinic anhydride, thereby fully revealing its constitution as 1:2- β -

naphthapyrone-8-acetic acid. The following scheme explains the reactions involved.



This observation has thus proved to be of great interest and value on account of the light it throws on the constitution of the coumarins arising from β -naphthol. It indicates very clearly that it is the hydrogen atom in 1 and not that in the 3 position of β -naphthol, which participates in the reaction with β -ketonic esters under the conditions of Pechmann's condensation, and as a consequence, confirms the structures previously assigned to 4-methyl- β -naphthacoumarin (m.p. 179°) and β -naphthacoumarin-4-acetic acid (m. p. 191°).

Considerable amounts of the dicoumarin, 3:8-di-1:2- β -naphthapyrone, were also formed in the reaction between β -naphthol-aldehyde and sodium succinate, according to the following equation.



EXPERIMENTAL.

Condensation of β -naphthol and malic acid.—A mixture of β -naphthol (14.4 g.) and malic acid (12.5 g.) was heated on wire gauze with concentrated sulphuric acid (30 c. c.). In the initial stages of heating, the liquid mixture, for some unexplained reason, completely solidified. It liquefied again on continuing the heating, and after a short time, began to evolve carbon monoxide. As soon as the mixture commenced frothing vigorously, the burner was removed and the reaction allowed to complete of itself. The cold dark red melt was mixed with cracked ice (500 g.) and allowed to stand for 4 hours. The main bulk of the deeply coloured solution was decanted from the very fine solid which had settled to the bottom, and the latter separated from the small amount of mother-liquor by centrifuging, the fineness of the particles making filtration almost impossible. The solid was washed by stirring with small volume of water, again centrifuged, dried and powdered. A bright orange yellow crystalline powder with a splendid metallic sheen was thus obtained, weighing approximately 0.6 g. It showed no signs of melting even when heated to 320°. The substance hardly dissolved in alcohol, benzene, etc., and could not therefore be crystallised from these solvents. When triturated with excess of water it went into an opalescent, colloidal solution, having a deep orange colour, which became instantly clear and colourless on adding a few drops of dilute alkali or alkali carbonate solutions.

The filtrate from the above was extracted four times with ether, the green fluorescent ether extract evaporated to dryness, and the brownish solid residue rubbed for a few minutes with 2 p. c. caustic soda, and filtered. It was finally crystallised twice from 50 p. c. alcohol in pale yellow needles (m.p. 118°); yield, nearly 1 g. There was no depression of its melting point when mixed with a specimen of the β -naphthacoumarin (m.p. 118°) prepared by Kauffman's method. The identity of the substance with Kauffmann's coumarin was further confirmed by converting it into the *trans*-o-coumaric acid by heating with sodium sulphite and alkali according to the method of Dey and Row (*J. Chem. Soc.*, 1924, 125, 554). Both of them yielded the same acid, m.p. 165° (decomp.).

Action of sodium succinate and succinic anhydride on 2-naphthol-1-aldehyde: Formation of 1:2- β a-naphthapyrone-3-acetic acid, and 3:3-di-1:2- β a-naphthapyrone.— β -Naphthol-aldehyde (7g.) and sodium

succinate dried at 140° for 3 hours (7 g.) are intimately mixed with freshly made succinic anhydride (14 g.) and heated under air reflux on an oil-bath at 180° for 5 hours. On cooling, the hard mass was broken up and left in contact with a solution of sodium carbonate (17 g. in 50 c.c.) for 12 hours. The reddish solution was filtered from the insoluble residue, the filtrate carefully acidified with HCl, and the brown coloured precipitate collected, washed and dried. It melted at $250-55^{\circ}$, and weighed 3.8 g. It was insoluble in water and dissolved very sparingly in alcohol but more readily in hot glacial acetic acid. A single crystallisation from the latter solvent raised the melting point to 264° , not depressed by admixture with the product obtained from β -naphthol and ethylformyl succinate (Dey and Sankaranarayanan, *loc. cit.*). (Found: M. W., (by titration with N/10 alkali), 251. $C_{15}H_{10}O_4$ requires M.W., 254).

The methyl ester, prepared in the usual manner, melted at 149° , and was identified with the methyl ester of the corresponding acid obtained from ethylformyl succinate.

The insoluble residue which had a dark yellow colour was left in contact with N-alkali (50 c.c.) for 2 hours, filtered, and the residue thoroughly washed with cold water. The clear filtrate, on acidification, deposited a small quantity of an impure tar which could not be investigated further. The yellow residue still melted indefinitely ($270-90^{\circ}$); it was purified by boiling for 5 minutes with N/2-alkali (50 c.c.), and quickly filtering the hot solution. Two such washings raised the melting point of the crude product to 380° , yield 1.9 g. (approx.). It was practically insoluble in alcohol, benzene, acetic acid and the other common organic solvents; it dissolved sparingly in boiling pyridine and more readily in hot nitrobenzene, and was finally crystallised from the latter solvent and washed with hot alcohol. Beautiful golden yellow needles, m.p. 345° , yield 1.4 g. (Found: C, 79.27; H, 3.79. $C_{26}H_{14}O_4$ requires C, 80.0 H, 3.59 per cent.).

On a New Method of Preparation of Hexammine-tri-ol-dicobalti-chloride and the Preparation of some Nuclear Polymers.

BY TUHINANGSU DAS-GUPTA AND PULIN BIHARI SARKAR.

Both from our work on the thiosulphato-aquo-tetrammine-cobaltic salts (*J. Indian Chem. Soc.*, 1930, 7, 835), and that of Ray on the thio-sulphato-pentammine-cobaltic series (*J. Indian Chem. Soc.*, 1927, 4, 64) it is apparent that S_2O_3 radicle takes up one co-ordination position only in the cobaltamine complexes.

Attempt was made to introduce S_2O_3 radicle within the complexes of the triammine series. Our starting material was according-

ly the dichrocobaltic salt, $\left[\begin{array}{c} Cl_2 \\ Co(NH_3)_3 \\ H_2O \end{array} \right] Cl$ which was obtained

by the action of concentrated hydrochloric acid on $\left[Co \begin{array}{c} (NO_2)_3 \\ (NH_3)_3 \end{array} \right]$ by the method of Jørgensen (*Z. anorg. Chem.*, 1898, 17, 475).

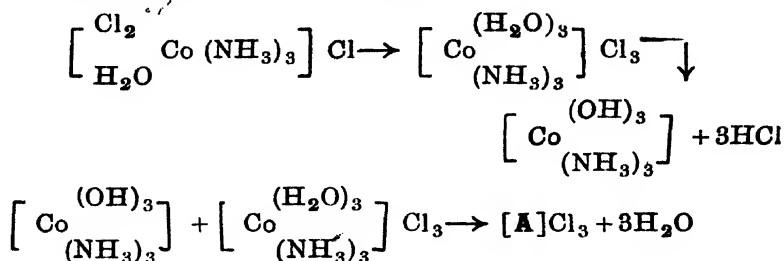
Reaction with sodium thiosulphate gave rise to the decomposition of the complex even at low temperatures with the formation of a very small amount of a red salt which was proved to be tetrahydrated hexammine-tri-ol-dicobalti-thiosulphate. The triammine cobaltic salts are generally very unstable, on the other hand, the condensation product of the triammines, which have very little been studied, are much more stable. Werner obtained a series of brownish red

salts of the formulæ $\left[(NH_3)_3 Co \begin{array}{c} \diagup OH \\ -OH- \\ \diagdown OH \end{array} Co(NH_3)_3 \right] X_3$ by

(A)

careful addition of dilute caustic soda on the dichrocobaltic chloride. The yield as pointed out by him is too small for practical utility and the maximum yield obtained by him is 0.5 g. from 5 g. of the dichrosalt ; cf. E. Birk (*Z. anorg. Chem.*, 1928, 175, 405) who has also by a modification of Werner's method using caustic potash and excess of ammonium chloride instead of caustic soda been able to increase the yield from 0.5 to 1.8 g.

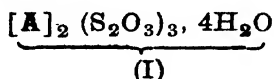
As regards the mechanism of the formation of the condensation product Werner assumed the following.



If the above mechanism is to be assumed it naturally follows that the hydrolysis and the subsequent removal of the free acid is the prominent factor in bringing about this coupling. Werner, therefore, added the calculated amount of caustic soda very carefully from a burette, the temperature being kept low.

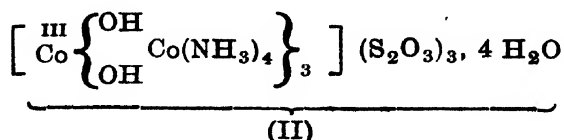
It suggested to us that if we can use a suitable reagent which will favour the hydrolysis and keep the solution at proper p_{H} , better yield of this condensation product would be expected. We, accordingly, used instead of caustic soda, hexamethylenetetramine and have been able thereby to increase the yield from 0.5 g. of Werner to 2.5 g. We have thus found a new method of preparation of the hexammine-tri-ol-dicobalti salts.

From the hexammine-tri-ol-dicobalti salts, which is much more stable than its parent dichro-cobalt salt, by double decomposition with sodium thiosulphate, the hexammine-tri-ol-dicobaltic thiosulphate of the formula (I) is obtained.



By the action of sodium thiosulphate, which is also hydrolysing agent, on dichrocobalt chloride, a very small amount of red salt was obtained which was found to be identical with the above compound.

By double decomposition of dodecammine-hexol-tetracobaltic nitrate with sodium thiosulphate a black salt of the formula (II) is obtained



which is a co-ordination isomer of the red salt (I).

EXPERIMENTAL.

Preparation of the hexammine-tri-ol-dicobaltic chloride.—Werner (Ber., 1906, 39, 2674 ; Werner and Grün, *ibid.*, 1907, 40, 4834) first prepared the above compound by careful addition of calculated amount of NaOH on dichrocobalt chloride. The yield obtained by him was only 12.5 p. c. of the theoretical, whereas by the following procedure we obtained 62.5 p. c. of the theoretical yield.

5 G. of the dichloro-aquo-triammine cobaltic chloride (known as the dichro-cobalt-chloride) were moistened with 5 c.c. of water in a small beaker and the mixture was heated over a tiny flame till complete mixing was effected. To the above solution, 1.5 g. of 'urotropine' was added and the temperature was raised to 45° by keeping the mixture for a few minutes on a hot water-bath. It was then removed from the water-bath and quickly filtered under suction. The red thick liquid thus obtained was placed in a freezing mixture of ice and salt. Brownish-red needle shaped crystals were obtained. The yield of the crude product was 2.9 g. This was purified by dissolving in 10 c.c. of water by careful heating on the water-bath. The solution was filtered and absolute alcohol was added drop by drop until turbidity appeared. It was again dissolved to a clear liquid on warming. The filtered solution began to crystallise on cooling, yield 2.5 g. (Found: Co, 29.72 ; NH₃, 25.57 ; Cl, 27.04. [A] Cl₃, H₂O requires Co, 29.83 ; NH₃, 25.79 ; Cl, 26.90 per cent.).

Preparation of hexammine-tri-ol-dicobaltic thiosulphate.—4 G. of the hexammine-tri-ol-dicobaltic chloride were dissolved in 20 c.c. of water and to the clear filtered solution, powdered sodium thiosulphate (4 g.) was added and the whole vigorously stirred. A dull red product was obtained. It was drained, first washed with cold water, then with dilute alcohol and finally with absolute alcohol. The yield is 2.5 g. The product is insoluble in water. (Found: Co, 24.69 ; S, 20.88 ; NH₃, 21.8. Formula (I) requires Co, 24.84 ; S, 20.21 ; NH₃, 21.47 per cent.).

Preparation of dodecammine-hexol-tetracobaltic-thiosulphate.—Diaquo-tetrammine-cobaltic nitrate obtained from the carbonate-tetrammine salt is acidic in aqueous solution. When it was neutralised with NaOH or KOH and kept in air, shining black crystals of dodecammine-hexol-tetracobaltic nitrate are obtained. Dodecammine-hexol-tetracobaltic-nitrate has been prepared by adding pyridine to a hot dilute acetic acid solution of diaquo-tetrammine-cobaltic

nitrate according to the method of Werner (*Ber.*, 1907, **40**, 2108). (Found: Co, 25.93 ; NH_3 , 22.16. Dodecammine-hexol-tetracobalti-nitrate requires Co, 25.82 ; NH_3 , 22.32 per cent.).

4.5 G. of dodecammine-hexol-tetracobalti-nitrate were dissolved in 25 c.c. water and 2.5 g. of powdered sodium thiosulphate were added to the solution and stirred. A black crystalline substance was obtained. It was drained, washed first with cold water in which it was almost insoluble and finally with absolute alcohol. The yield was 3 g. (Found: Co, 24.61 ; S, 20.30 ; NH_3 , 21.33. Formula (II) requires Co, 24.84 ; S, 20.21 ; NH_3 , 21.47 per cent.).

It is interesting to observe that the black crystalline dodecammine-hexol-tetracobalti-thiosulphate and the red crystalline hexamine-tri-ol-dicobaltic thiosulphate are two co-ordination polymers.

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Some New Hydrocupreidine Derivatives. Part II.

BY SUDHAMOY GHOSH AND NIHAR RANJAN CHATTERJEE.

In continuation of our previous paper (*J. Indian Chem. Soc.*, 1981, 8, 257) in which some *isoalkyl* derivatives of hydrocupreidine were described, the present paper deals with the preparation and properties of the corresponding and other *n*-alkyl derivatives of the same base. The therapeutic values of these derivatives are being studied. *iso*B utyl hydrocupreidine, which previously failed to crystallise, has now been included in the paper.

EXPERIMENTAL.

The *n*-alkyl hydrocupreidines and their hydrochlorides described below were prepared, except where otherwise mentioned, in the same way as the *isoalkyl* hydrocupreidines (*loc. cit.*).

n-Propylhydrocupreidine.—It is soluble in alcohol, ether and benzene. It crystallised from acetone in thin long, colourless needles, m.p. 182°. $[\alpha]_D^{25} = +206.25^\circ$ ($c=1$ in chloroform). It gives a bluish fluorescence with dilute sulphuric acid. Yield, 1.9 g. from 6 g. of hydrocupreidine. (Found: N, 8.04. $C_{22}H_{30}O_2N_2$ requires N, 7.90 per cent.).

n-Propylhydrocupreidine hydrochloride crystallised from water as long, colourless needles, m.p. 222° (decomp.). It is readily soluble in water and alcohol. $[\alpha]_D^{25} = +227.5^\circ$ ($c=1$ in water). (Found: Cl, 16.23. $C_{22}H_{30}O_2N_2, 2HCl$ requires Cl, 16.60 per cent.).

n-Butylhydrocupreidine crystallised from moist acetone in colourless needles, m.p. 176°. It is soluble in absolute alcohol, ether, chloroform and benzene. It gives a bluish fluorescence with dilute sulphuric acid. $[\alpha]_D^{25} = +194.5^\circ$ ($c=1$ in chloroform). Yield, 2 g. from 6.26 g. of hydrocupreidine. (Found: N, 7.41. $C_{23}H_{32}O_2N_2$ requires N, 7.60 per cent.).

n-Butylhydrocupreidine hydrochloride crystallised from water in colourless needles. It is soluble in water and alcohol and melts with

decomposition at 226° to a dark brown liquid. $[\alpha]_D^{26} = +215^{\circ}$ ($c=1$ in water). (Found: Cl, 16.04. $C_{23}H_{32}O_2N_2 \cdot 2HCl$ requires Cl, 16.08 per cent.).

n-Amylhydrocupreidine crystallised from acetone in long colourless needles, m.p. 164° . It is soluble in absolute alcohol, ether, chloroform and benzene. It gives a bluish fluorescence with dilute sulphuric acid. $[\alpha]_D^{21} = +189.25^{\circ}$ ($c=1$ in chloroform). (Found: N, 7.24.

$C_{24}H_{34}O_2N_2$ requires N, 7.33 per cent.). Yield, 3.15 g. from 6.26 g. of hydrocupreidine.

n-Amylhydrocupreidine hydrochloride crystallised from water in silky needles, m.p. 223° . It is soluble in water and alcohol. $[\alpha]_D^{\circ} = +212.5^{\circ}$ ($c=1$ in water). (Found: Cl, 15.33. $C_{24}H_{34}O_2N_2 \cdot HCl$ requires Cl, 15.58 per cent.).

n-Heptyl hydrocupreidine crystallised from acetone in long, colourless, silky needles, m.p. 158° . It is soluble in alcohol, chloroform ether and benzene. It gives a bluish fluorescence with dilute sulphuric acid. $[\alpha]_D^3 = +179.75^{\circ}$ ($c=1$ in chloroform). (Found: N, 6.87. $C_{26}H_{38}O_2N_2$ requires N, 6.82 per cent.). Yield, 2.5 g. from 6.26 g. of hydrocupreidine.

n-Heptylhydrocupreidine hydrochloride crystallised from water in colourless needles, m.p. 215° . It is readily soluble in absolute alcohol but less soluble in cold water. $[\alpha]_D^{20} = +195^{\circ}$ ($c=1$ in $N/50$ HCl). (Found: Cl, 14.78. $C_{26}H_{38}O_2N_2 \cdot 2HCl$ requires Cl, 14.68 per cent.).

n-Octylhydrocupreidine.—As the hydrochloride of this base was very sparingly soluble in water, the method of isolation from the reaction product was slightly different. After the reaction, the mixture was cooled and poured into water when the base soon separated out on stirring as a brown powder. The mother-liquor was kept strongly alkaline by the addition of caustic soda so as to dissolve the unchanged hydrocupreidine and left overnight. It was then filtered, washed and dried. It crystallised from acetone in thin needles. It was also found that the molecular copper which was used as catalyst deposited on the walls of the reaction flask as a mirror. It seems that the copper went into combination during the reaction and was afterwards liberated as such. The base melts at 151° to a brown liquid. It is soluble in absolute alcohol, chloroform, ether and benzene. It gives a bluish fluorescence with dilute sulphuric acid.

$[\alpha]_D^{21} = +170.75^\circ$ ($c=1$ in chloroform). (Found : N, 6.65, $C_{27}H_{40}O_2N_2$ requires N, 6.60 per cent.). Yield, 8.85 g. from 6 g. of hydrocupreidine.

n-Octylhydrocupreidine hydrochloride crystallised from hot water in colourless, silky needles, m.p. 210° . It is soluble in hot water and alcohol and sparingly so in cold water and acetone. $[\alpha]_D^{21} = +182.5^\circ$ ($c=1$ in $N/10$ HCl). (Found : Cl, 13.81. $C_{27}H_{40}O_2N_2, 2HCl$ requires Cl, 14.26 per cent.).

isoButyl hydrocupreidine crystallised well from acetone in colourless needles, melting at 175° . It is soluble in alcohol, ether and benzene. $[\alpha]_D^{20} = +186.7^\circ$ ($c=2$ in chloroform). It gives a bluish fluorescence with dilute sulphuric acid. (Found : N, 7.38. $C_{23}H_{32}O_2N_2$ requires N, 7.60 per cent.).

In conclusion, we desire to express our grateful thanks to Lt. Col. H. W. Acton, C.I.E., at whose suggestion we took up the work, for affording all the facilities for carrying it out.

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A Note on the Calculation of the Space Displacements of Terminal Carbon Atoms in Ring Formation.

By K. R. GUNJIKAR AND T. S. WHEELER.

Short (*Chem. News*, 1926, 133, 149) points out that in certain cases a good measure of the tendency to ring formation of a uniplanar polymethylene chain is given by what he calls the "approach value". This conception was first introduced by Ingold (*J. Chem. Soc.*, 1921, 119, 307), whose definition is, however, rather vague. He merely refers to his values as showing "by how much" the terminal carbon atoms of a normal polymethylene chain must approach one another in forming the corresponding uniplanar cycloparaffin ring. An examination of his results indicates that, taking as the unit, the distance between two adjacent carbon atoms in the unstrained chain, the "approach value" is half the difference in the distance between the terminal carbons before and after displacement.

Approach values have been calculated for special cases by Ingold and Short, but the general formula relating them to the valency angle (*i.e.*, the angle between each pair of carbon-to-carbon valencies in the unstrained chain), and to the number of carbon atoms in the chain, has not yet been given. The derivation of the formula is shown in what follows.

The general formula for approach values.—Consider an unstrained chain with n methylene groups, and join without displacement the terminal carbon atoms 1 and n . Let a be the distance between the adjacent carbon atoms in the chain, and let $2\theta^\circ$ be the valency angle.

If $(1, n)$ is the distance between the terminal carbon atoms before ring formation, then half the difference in the distances between the terminal carbon atoms before and after displacement is

$$\frac{(1, n) - a}{2}$$

and since the approach value is this quantity when a is taken to be the unit of distance, we have, approach value

$$= \frac{(1, n) - a}{2a}.$$

The angle between $(1, n)$ and $(1, 2)$ is given by

$$\left[\frac{(n-1)(180) - 180 - 2\theta(n-2)}{2} \right]^\circ = (90 - \theta)(n-2)^\circ.$$

This can be seen by joining any point O in $(1, n)$ to all the carbon atoms, and considering the angles of the $(n-1)$ triangles so formed. The sum of these angles amounts to $(n-1)(180)^\circ$. From this must be deducted the angle of 180° at O , and also $(n-2)$ angles each equal to $2\theta^\circ$, in order to obtain the sum of the two equal angles between $(1, n)$ and, respectively, $(1, 2)$ and $(n-1, n)$.

The angle between $(1, n)$ and $(2, 3)$ is

$$[(90 - \theta)(n-2) - (180 - 2\theta)]^\circ = (90 - \theta)(n-4)^\circ.$$

Proceeding in this way we obtain,

$$(1, n) = a [\cos (90 - \theta)(n-2)^\circ + \cos (90 - \theta)(n-4)^\circ + \dots + \cos (n-2)^\circ] = \frac{a \sin (n-1)(90 - \theta)^\circ}{\cos \theta^\circ}.$$

From which we have, approach value

$$= \frac{(1, n) - a}{2a} = \frac{\sin (n-1)(90 - \theta)^\circ}{2 \cos \theta^\circ} - 0.5. \quad \dots (1)$$

This general formula yields the values given by Ingold and Short for the particular cases they considered.

Thus for $2\theta = 115.3^\circ$, the valency angle assumed by Ingold, and $n=4$, we have, approach value

$$= \frac{\sin (4-1)(90 - 57.6)^\circ}{2 \cos 57.6^\circ} - 0.5 = \frac{\sin 97.2^\circ}{2 \cos 57.6^\circ} - 0.5$$

$$= \frac{.992}{1.07} - 0.5 = .427$$

which agrees with the value given by Ingold.

Since the general formula for the angle of strain is

$$\alpha^\circ = \left[\frac{\theta - 90(n-2)}{n} \right]^\circ, \quad \dots (2)$$

it is clear from a comparison of (1) and (2), that there is no simple relation between α and the approach value. Accordingly the comparison made by Ingold (*loc. cit.*) between the heats of formation of a series of cycloparaffin rings, the Baeyer values for α , and the approach values calculated from the Ingold value for θ , is meaningless and cannot lend support to any theory. Short (*loc. cit.*) has in fact shown by calculation that the approach values calculated from the Baeyer value of θ are in as good functional agreement with the thermal values as those calculated from Ingold's value of θ .

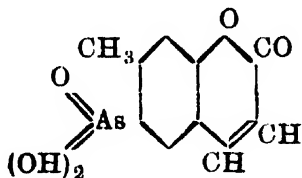
The discussion has here been confined to uniplanar rings. Ruzicka and his collaborators have shown (*Helv. Chim. Acta*, 1926, 9, 230, 249, and subsequent papers) that polymethylene rings containing a large number of carbon atoms can be formed, strain being relieved by the rings ceasing to be uniplanar. We hope to investigate the general conditions under which the approach value for a multiplanar ring can become zero. This involves complete removal of strain.

Introduction of Arsenic into Coumarin Nucleus.

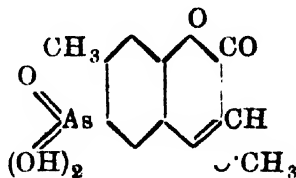
Part II.

BY M. GOSWAMI AND H. N. DAS-GUPTA.

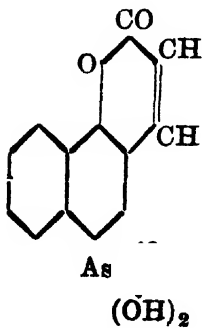
It has already been pointed out in our previous communication (*J. Indian Chem. Soc.*, 1931, 8, 417) that the groups-O-CO- and -CH=CH- present in coumarin nucleus together with arsenic might prove to have some effect in the treatment of tuberculosis. The present paper deals with certain new substituted coumarins and naphthacoumarins containing the same therapeutically active components in the nucleus. The following compounds are described in the present paper: 7-methylcoumarin-5-arsinic acid [?](I), 4:7-dimethylcoumarin-6-arsinic acid (II), 1:2- α -naphthapyrone-6-arsinic acid (III) and 4-methyl-1:2- α -naphthapyrone-6-arsinic acid (IV).



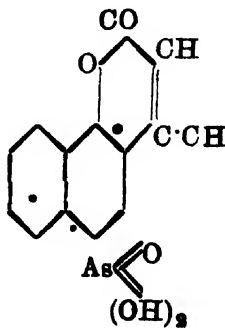
(I)



(II)



(III)



(IV)

These have been prepared from their amino derivatives by Bart's reaction and unlike the arsenic derivative of coumarin (*loc. cit.*),

they all gave monoderivatives. Attempts to introduce arsenic into 8-amino-4-methyl-7-hydroxycoumarin and 8-amino-4-methyl-7-methoxycoumarin were not successful.

It appears that no attempt has yet been made to nitrate 1:2- α -naphthapyrone. The compound was nitrated by a mixture of fuming nitric acid and acetic acids. The position at which the nitro group entered the nucleus was supposed to be "6" from an analogy of the other nitro derivatives of coumarin.

The arsenic compounds described are generally light yellow in colour and dissolve very easily in caustic alkalis and alkali carbonates from which hydrochloric acid precipitates the original compounds.

EXPERIMENTAL.

7-Methylcoumarin-6-arsinic acid.—7-Methyl-6-aminocoumarin (4 g.) was dissolved in a mixture of hot water (30 c.c.) and hydrochloric acid (6 c.c.) and the mixture was heated to boiling and then suddenly cooled to 0°, the object being to obtain the sparingly soluble hydrochloride in a fine state of division. The amino compound was then diazotised in the usual manner using a solution of sodium nitrite (2 g.) in water (10 c.c.) and the diazo solution gradually added to well cooled alkaline solution of sodium arsenite prepared from sodium carbonate (8 g.) arsenious acid (3 g.) water (100 c.c.) and copper sulphate (16 g.) as catalyst, and the whole mass was kept well stirred during the operation. The stirring was continued for one hour more after the addition of the diazo solution. The separated tarry and insoluble matters were filtered off. The filtrate concentrated to a low bulk, boiled with animal charcoal and filtered hot. It was then cooled to the room temperature and concentrated hydrochloric acid was gradually added till the precipitated compound dissolved in excess of the strong acid in which it is soluble. At this stage the solution was again filtered from the tarry and insoluble matters, the filtrate rendered alkaline and the arsenic compound was precipitated with careful addition of dilute hydrochloric acid as yellowish white stuff. The repetition of the above process gave the compound in a sufficiently pure condition, m.p. 290° (decomp.). (Found: As, 26.0. $C_{10}H_9O_5As$ requires As, 26.4 per cent.).

4,7-Dimethyl-6-arsinic acid.—4:7-Dimethyl-6-aminocoumarin (2.2 g.) was dissolved in a mixture of hydrochloric acid (2.5 g.) and water (20 c.c.) and diazotised in the same manner as stated above with a solution of sodium nitrite (.9 g.) in water (10 c.c.). This was gradually added to a well stirred sodium arsenite solution made of sodium carbonate (4 g.), arsenious oxide (1.5 g.), copper sulphate (.07 g.) and water (60 c.c.). The resulting product was filtered, concentrated, boiled with animal charcoal and again filtered. The filtrate was cooled and then gradually acidified with hydrochloric acid when cream coloured precipitate of arsenic derivative was obtained. The precipitate was separated by filtration, purified as in the previous case, washed with hot water and then dried in a vacuum desiccator; m.p. 285° (decomp.). (Found: As, 24.8. $C_{11}H_{11}O_5As$ requires As, 25.3 per cent.).

6-Nitro-1:2-*a*-naphthapyrone.—1:2-*a*-Naphthapyrone (43 g.) was dissolved in hot glacial acetic acid (100 c.c.). To this hot solution, nitric acid (15 c.c. d 1.52) was gradually added. The whole was then heated on the water-bath with constant stirring and the heating continued till the crystals of the nitro compound appeared. At this stage the product was poured upon pounded ice when dark yellow nitro derivative separated. This was filtered, washed free from acid and crystallised from acetone in yellow microcrystalline powder, m.p. 180°, yield theoretical. (Found: N, 5.75. $C_{13}H_7O_4N$ requires N, 5.8 per cent.).

6-Amino-1:2-*a*-naphthapyrone.—6-Nitronaphthacoumarin (24 g.) was gradually added to a warm clear solution of stannous chloride (70 g.) in a mixture of hydrochloric acid (60 c.c.) and alcohol (50 c.c.). The reduction was over when every thing went into solution. More hydrochloric acid (120 c.c.) was now added and the solution allowed to cool when the hydrochloride of the base separated out. It was filtered, washed thoroughly with concentrated hydrochloric acid, dissolved in hot water and treated with a hot solution of sodium acetate when the base was liberated as golden yellow crystals, m.p. 194°, yield 60 per cent.

***a*-Naphthapyrone-6-arsinic acid.**—This was prepared from 6-amino-1:2-*a*-naphthapyrone as above. It was obtained as yellow microcrystalline powder from alcohol not melting even upto 360°. The yield was very low. (Found: As, 22.9. $C_{13}H_9O_5As$ requires As 28.4 per cent.).

4-Methyl-1:2-a-naphthapyrone-6-arsinic acid.—It was prepared from 6-amino-4-methyl-1:2-a-naphthapyrone and purified in a similar way and crystallised from acetic acid as a yellowish white microcrystalline powder. The acid shrinks at 340° but does not melt even at 360°. (Found: As 22·3. $C_{14}H_{11}O_5As$ requires As 22·4 per cent.).

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A New Method of Estimating Arsenic in Organo-arsenic Derivatives. Part I.

BY HIRENDRA NATH DAS-GUPTA.

The application of organic derivatives of arsenic as drugs, has brought into prominence the problem of estimating the metalloid, when directly combined with carbon. A survey of the references given in the foot-note, will clearly explain the fact that each author by adopting a new method or some modifications of the older ones aimed at getting an inorganic derivative of arsenic either by dry or moist combustion of the organic compound, the arsenic being subsequently estimated either gravimetrically or volumetrically.

A method of estimating arsenic in organic tissues, devised by Norton and Koch (*loc. cit.*) has been successfully utilised in the estimation of the metalloid in its organic derivatives by Ewins (*J. Chem. Soc.*, 1916, 109, 1356). The method has its universal application but suffers from the main drawback that the end point is never sharp and that the experiment is attended with vigorous frothing at the outset which can be controlled only with difficulty.

In course of some experiments on the problem of introducing pentavalent arsenic into therapeutically active organic compounds, the author's attention was drawn to the fact that with the exception of a very few, majority of the organo-arsenic acids are soluble in hydrochloric acid. Anticipating that the arsenic, which is in its highest state of oxidation in such compounds, should liberate an equivalent amount of iodine in presence of hydrochloric acid from a solution of potassium iodide, pure phenylarsinic acid was treated in a similar

La Coste and Michaelis, *Annalen*, 1880, 201, 224; Gooch and Browning, *Amer. J. Sci.*, 1890, iii, 11, 66; Little, Cahen and Morgan, *J. Chem. Soc.*, 1909, 95, 1478; Pringsheim, *Amer. Chem. J.*, 1904, 31, 386; Monthule, *Ann. chim. Anal.*, 1904, 9, 308; Morgan, *J. Chem. Soc.*, 1904, 85, 1001; Norton and Koch, *J. Amer. Chem. Soc.*, 1905, 27, 1247; Martindale, *Extra Pharmacopoeia*, 1915, 11, 27; Kircher and Rupert, *Ber. Deut. Pharm. Ges.*, 1920, 30, 419, 421; Newbery, *J. Chem. Soc.*, 1925, 127, 1751; R Stolle and O Fechtig, *Ber. Deut. Pharm. Ges.*, 1923, 33, 59; Kolthoff, *Z. Anal. Chem.* 1923, 62, 137, 38.

way. The analytical results obtained proved the correctness of the assumption. This gave a clue to an easier way of estimating the pentavalent arsenic in organo-arsenic acids as the liberated iodine may easily be titrated by means of sodium thiosulphate. The method is very rapid (from fifteen to twenty minutes for the estimation) and gave accurate results with the compounds enumerated below. A few of the typical organo-arsenic derivatives belonging to different groups have been examined. The advantages of the method are that it requires only a very small quantity (from ten to fifteen mg.) of the substance and requires only simplest apparatus and materials. Organo arsenic acids that are insoluble in hydrochloric acid are, first of all, brought into solution by heating with glacial acetic acid and then treated with hydrochloric acid and potassium iodide solution. A compound of this type viz., naphthylarsinic acid (Hill and Balls, *J. Amer. Chem. Soc.*, 1922, **44**, 2051) has been tried with success.

The following table summarises the experimental results of the present investigations.

EXPERIMENTAL.

Substance.	Quantity.	Arsinic content.	
		Found.	Calc.
Ethylarsinic acid	·0286 g	48·28	48·7 per cent.
	·0170	48·19	
Phenylarsinic acid	·0178	37·2	37·1
	·0146	37·1	
	·0201	37·09	
Benzylarsinic acid	·0218	34·69	34·7
	·0252	34·78	
Nephthylarsinic acid	·0126	29·1	29·7
	·0101	29·08	
Tricoumarylarsinic oxide	·0225	14·16	14·2
	·0199	14·09	
7-Methylcoumarin-6-arsinic acid	·0116	26·1	26·4
	·0124	26·08	
4:7-Dimethylcoumarin-6-arsinic acid	·0110	25·25	25·3
	·0221	25·2	
Naphthacoumarin-6-arsinic acid	·0204	23·25	23·4
	·0199	23·3	
4-Methylnaphthacoumarin-6-arsinic acid	·0193	22·45	22·4
	·0265	22·5	

Procedure—A small quantity of the substance (0.01 to 0.02 g.) was weighed out accurately in a conical flask of about 500 c. c. capacity. Concentrated hydrochloric acid (15 c.c. *d* 1.19) was run in and the whole heated on a water-bath for five minutes. In case an uniform solution is not obtained, the mixture should be heated by direct flame. The solution was cooled to the room temperature and glacial acetic acid (15 c.c.) and water (50 c.c.) were then added. In a separate beaker potassium iodide (4 g.) dissolved in water (10 c.c.) was added to the acid solution. The solution assumed a brown or yellow coloration due to the liberation of free iodine. The walls of the flask were then washed with a little water and the liberated iodine titrated against *N*/20 sodium thiosulphate solution. Towards the end of the titration 2 c.c. of a one per cent. solution of starch was added and the titration continued to the end. After the point at which the blue coloration, due to free iodine and starch, faded away which however was not the exact end point, the thiosulphate solution was carefully added drop by drop with constant stirring till the original colour of the solution of the substance in hydrochloric acid was attained.

From the amount of thiosulphate solution required, the percentage of arsenic present is easily calculated. One c.c. of *N*/20 thiosulphate solution \equiv 0.0000375 g. of arsenic.

Experiments with other derivatives of arsenic, in the tri-valent state, are in progress.

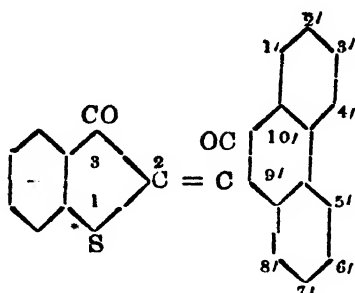
In conclusion I wish to express my gratitude to Dr. M. Goswami, for his kind interest and valuable suggestions in this investigation.

Indigoid Dyes Derived from Phenanthraquinone. Part I. Thionaphthene-phenanthrene Indigos.

BY PARESH CHANDRA DUTTA.

It has been shown by Friedlander, Herzog and Voss (*Ber.*, 1922, 55, 1591) that phenanthraquinone condenses very easily with 3-hydroxythionaphthene in acetic acid solution containing traces of hydrochloric acid and a violet dye is produced. Later on Luther (*Ber.*, 1931, 64, 881) prepared the same substance in a pure crystalline form by a slight modification of the above method. The present author got the substance as a chocolate brown crystalline mass and he has further extended this reaction to study the effect of different elements or groups on the colour of the substances. The condensation products with bromo- and nitrophenanthraquinones are violet in colour whereas those with amino- and hydroxyphenanthraquinones, black or brownish black. The substances dissolve in concentrated sulphuric acid with a green, violet green or violet brown colour and the original dyes are reprecipitated by treatment with water. The freshly precipitated compounds are found to be quite suitable for dyeing on wool from an acid bath, yielding even and deep shades. Except the bromo compounds which are very feebly soluble, they dissolve in hydrosulphite vat with a yellowish brown colour from which the original substances are reprecipitated by oxidation with air. The shades obtained on cotton from hydrosulphite vat were not very deep, but quite even and fast. Generally speaking, these substances are sparingly soluble in alcohol, moderately so in amyl alcohol and acetic acid and easily soluble in nitrobenzene, xylene and pyridine and they generally melt above 295° and some of them sublime at higher temperatures, yielding a reddish violet vapour. In the monosubstituted phenanthraquinones, it has not been determined which, of the two ketonic groups, actually, takes part in the reaction. Further work in this line is in progress.

The structure of these compounds can be represented by the following general formula.



For the sake of abbreviation, the preparation of only one of these compounds is given in the experimental portion, the rest being prepared in similar manners, their properties are recorded in the Table.

EXPERIMENTAL.

2-Thionaphthene- 9'(2'-nitro)-phenanthrene indigo.—Solutions of 2-nitrophenanthraquinone (1.26 g.) in hot acetic acid (100 c.c.) and 3-hydroxythionaphthene (0.8 g.) in 2 c.c. of the same solvent were freed from dissolved air by passing carbon dioxide and mixed together, thoroughly agitated and the mixture treated with 0.5 c.c. of hydrochloric acid in 5 c.c. of acetic acid. On boiling the mixture for ten minutes a brownish violet crystalline precipitate separated out. It was filtered hot and washed with a little acetic acid and then with alcohol. For purification, it was boiled with alcohol for sometime and filtered hot. The residue was dissolved in pyridine and reprecipitated as a violet crystalline precipitate by the cautious addition of hot water. It crystallises from amyl alcohol in small rectangular plates melting above 290°. It is sparingly soluble in alcohol, moderately in amyl alcohol and acetic acid and easily soluble in nitrobenzene, xylene and pyridine in the cold. It dissolves in concentrated sulphuric acid with a green colour and dyes wool in violet shades from an acid bath and dyes cotton in light violet shades from hydrosulphite vat.

Indigoid Dyes Derived from Phenanthraquinone.

Name.	Prepared from 3-hydroxy-T, and	Appearance.	Crystallised from	M.p.	Colour in strong sulphuric acid.	Shade on wool from acid bath.	Shade on cotton from hydro- sulphite vat.	Analysis.
								Found. Calcd.
2-T.9'-(2'-nitro)-PI	2-nitro-p	Violet crystalline mass.	pyridine	Above 290°	Green	Violet	Light violet	C, 64.23 68.57 H, 3.01 3.85
2-T.9'-(4'-nitro)-PI	4-nitro-p	"	"	"	"	Pinkish violet	Light pinkish violet.	C 68.38 68.57 H, 3.11 3.85
2-T.9'-(3' : 7'-dinitro)-PI	2 : 7-dinitro-p	"	"	"	"	Blackish violet	Light pink	N, 6.45 6.51
2-T.9'-(4' : 5'-dinitro)-PI	4 : 5-dinitro-p	"	"	"	"	Violet	"	N, 6.58 6.51
2-T.9'-(2'-bromo)-PI	2-bromo-p	Violet brown prismatic needles.	"	279°	Greenish brown	Reddish brown	—	Br, 18.91 19.09
2-T.9'-(dibromo)-PI	dibromo-p	Violet crystalline mass.	"	Above 295°	" violet	Violet	—	Br, 31.98 32.12
2-T.9'-(dibromonitro)-PI	dibromonitro-p	Violet needles.	"	Above 300°	Green	Deep violet	—	Br, 29.31 29.46
2-T.9'-(bromodinitro)-PI	bromodinitro-p	Deep violet prismatic needles.	nitro- benzene	281°	"	Violet blue	Pink	Br, 15.65 15.71
2-T.9'-(3' amino)-PI	2-amino-p	Violet brown microscopic needles.	pyridine	Above 295°	Greenish brown	Chocolate brown.	Light pink	C, 74.14 74.96 H, 3.81 3.66
2-T.9'-(4'-amino)-PI	4-amino-p	Black crystalline mass.	"	Above 300°	"	Deep violet	"	C, 74.08 74.96 H, 3.88 3.66
2-T.9'-(3' : 7'-diamino)-PI	2 : 7-diamino p	Blackish-brown crystalline mass.	"	"	Brown red	Chocolate brown	Light pinkish brown	N, 7.38 7.56
2-T.9'-(4' : 5'-diamino)-PI	4 : 5-diamino-p	Violet-black crystalline mass.	"	Above 295°	Violet black	Blackish violet	—	N, 7.24 7.56
2-T.9'-(2'-hydroxy)-PI	2-hydroxy-p	crystalline mass. Violet-black	acetic acid	200°	Bottle green	Violet	Violet	C, 73.86 74.15 H, 3.46 3.97
2-T.9'-(4'-hydroxy)-PI	4-hydroxy-p	Violet-brown needles.	"	Above 300°	Violet brown	Blackish brown	Blackish brown	C, 73.81 74.15 H, 3.57 3.37
2-T.9'-(2' : 7'-dihydroxy)-PI	2 : 7-dihydroxy-p	Brownish black plates.	"	"	"	Greenish brown	Greenish brown	C, 70.57 70.96 H, 3.45 3.23

In conclusion, the author takes this opportunity to express his hearty thanks to his friend Dr. S. C. De for his help and co-operation and to the Principal and his colleagues for the interest they had taken in this investigation.

CHEMICAL LABORATORY.

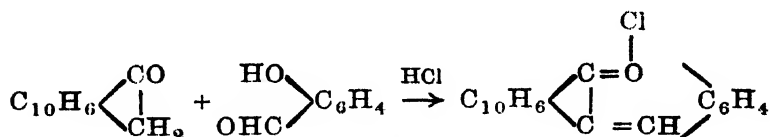
G. B. B. COLLEGE, MUZAFFARPUR (B. & O.).

Received February 6, 1932.

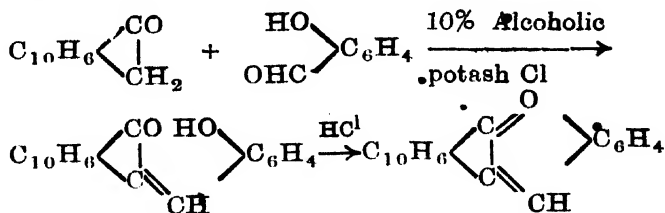
Studies in Acenaphthenone. Part I. Pirylium Derivatives.

BY ANUKUL CHANDRA SIRCAR AND M. D. RAJA GOPALAN.

Decker and Fellenberg (*Ber.*, 1907, **40**, 3815; *Annalen*, 1907, **356**, 281), Perkin, Robinson and Turner (*J. Chem. Soc.*, 1908, **93**, 1085), Pratt and Robinson (*J. Chem. Soc.*, 1922, **121**, 1577; *ibid.*, 1923, **123**, 743 etc.), De (*J. Indian Chem. Soc.*, 1927, **4**, 23, 137) and others have shown that *o*-hydroxyaldehydes can condense with substances containing the group-CH₂-CO-under certain conditions to form pyrylium compounds. It was therefore natural to expect that acenaphthenone which also contains the group-CH₂-CO-would yield pyrylium derivatives. This expectation has been amply rewarded by the preparation of pyrylium derivatives by the condensation of acenaphthenone with salicylic and β -resorcylic aldehydes. Condensations were effected in two different ways, *viz.*, (1) by passing gaseous hydrogen chloride through a glacial acetic acid solution of equimolecular quantities of the respective aldehydes and acenaphthenone (Decker and Fellenberg, *loc. cit.*),



(2) by first preparing the *o*-hydroxystyryl ketone by condensation of the aldehyde and acenaphthenone in alkaline solution and subsequently converting it into the pyrylium salt by the action of dry gaseous hydrogen chloride (Pratt and Robinson, *loc. cit.*).

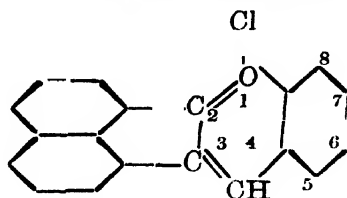


In the case of salicylic aldehyde, the free pyrylium chloride could not be isolated, as it decomposed immediately in contact with air. The corresponding ferri-chlorides and the perchlorates are, however, quite stable and were obtained in beautiful crystalline forms. In the

case of β -resorcylic aldehyde, in addition to the ferri-chloride and the perchlorate the free pyrylium chloride, which is quite stable, were also obtained.

EXPERIMENTAL.

2:3-Acenaphthbenzopyrylium Chloride.



Acenaphthenone (0.5 g.) and salicylic aldehyde (0.38 g.) were dissolved in glacial acetic acid (10 c.c.) and dry hydrochloric gas was passed through the solution for $1\frac{1}{2}$ —2 hours. The almost colourless solution gradually turned yellow and finally became orange yellow. The completion of the reaction was indicated when there was no further precipitation on the addition of a little of the reaction mixture to dilute hydrochloric acid. The solution was then poured into a large volume of ether and the yellow solid pyrylium chloride separated after some time. The ethereal layer was decanted off and the solid, after being quickly filtered and washed with ether, was kept in a vacuum desiccator. So long as the substance was in the desiccator it was solid, but on removal immediate decomposition set in with the liberation of hydrogen chloride gas and the solid became resinous. The solid is so unstable in air that it was not possible even to take the melting point. The solid is soluble in dilute hydrochloric acid (1:1) and glacial acetic acid. It is sparingly soluble in alcohol and insoluble in all other organic solvents.

2:3-Acenaphthbenzopyrylium ferri-chloride.—It was obtained as a dark yellow precipitate by adding ferric chloride, dissolved in concentrated hydrochloric acid into the glacial acetic acid solution of the pyrylium chloride described in the previous experiment. The addition of ferric chloride was continued until the precipitation was complete. It was then filtered and washed with moderately dilute hydrochloric acid, and finally with alcohol. It was obtained as yellow shining rectangular plates from boiling acetic acid. The crystals were dried over potash in a desiccator, m.p. 203° . It gives a straw yellow coloration with concentrated sulphuric acid from which it is not precipitated back on dilution. It decomposes when dissolved in water. It is insoluble in all organic solvents excepting acetic acid.

(Found: C, 51.04; H, 2.39. $C_{19}H_{11}O$, $FeCl_4$ requires C, 50.36; H, 2.43 per cent.).

2:3-Acenaphthbenzopyrylium perchlorate.—To the solution of 2:3-acenaphthbenzopyrylium chloride in glacial acetic acid, perchloric acid was added drop by drop until the separation of the crystals was complete. The separated shining yellow plates were filtered, washed first with glacial acetic acid and then with ether, and finally dried in the desiccator over potash. It melts at 255° with decomposition, and decomposes in presence of water. It gives a greenish yellow colour with concentrated sulphuric acid. (Found: C, 63.98; H, 3.50. $C_{19}H_{12}O_5Cl$ requires C, 64.13, H, 3.31 per cent.).

2:3-Acenaphthbenzopyrylium chloride. Second method).

(a) **Salicylidene acenaphthenone.**—Acenaphthenone (0.5 g.) and salicylic aldehyde (0.38 g.) were dissolved in the least quantity of alcohol and alcoholic potash (about 5 c.c. of 10 p.c.) added. The scarlet red solution obtained did not separate any precipitate even on standing. The solution was then poured into ether when a scarlet-red slimy precipitate was obtained which stuck to the sides of the vessel. The supernatant liquid was poured away and dilute hydrochloric acid added to the precipitate, when the colour changed to yellow. It was filtered, washed with water and crystallised from dilute alcohol in yellow needles, m.p. 186° .

(b) **Conversion of salicylidene acenaphthenone to the corresponding pyrylium chloride and the ferri-chloride.**—Salicylidene acenaphthenone (0.4 g.) was suspended in dry ether and dry hydrogen chloride gas passed through the suspension for about two hours. The solution gradually turned deep yellow and finally orange yellow. The pale yellow needles which were at the bottom gradually disappeared, and a dirty yellow amorphous powder separated. The completion of the reaction was indicated by the complete solubility of a sample in dilute hydrochloric acid after removal of ether. After the reaction was over, dilute hydrochloric acid was added to the mixture and ether distilled off. Care was taken to see that the concentration of the acid was sufficient to prevent hydrolysis of the oxonium salt. (1:1 HCl used). The solution was filtered and to the filtrate ferric chloride in concentrated hydrochloric acid added as in the previous preparation. The separated ferri-chloride was found to be identical with the one obtained previously.

7-Hydroxy-2:3-acenaphthbenzopyrylium chloride.—Acenaphthenone (1.5 g.) and β -resorcylic aldehyde (0.4 g.) were dissolved in

glacial acetic acid (8 c.c.) and dry hydrogen chloride gas passed through the solution. Reaction soon began as indicated by the change of the colour of the solution to deep red. On passing hydrogen chloride for about three hours deep red needles filled the whole liquid. The mixture was poured into a large excess of ether when whole of the solid got precipitated. This was filtered and washed with ether. The precipitate was then dissolved in hot dilute hydrochloric acid (1:1) and filtered hot to free it from any unreacted acenaphthenone. The filtrate, on cooling, deposited beautiful scarlet red needles, which were filtered and dried in a vacuum desiccator over potash. It melts at 181° . It is insoluble in almost all organic solvents but sparingly soluble in acetic acid. It dissolves in concentrated sulphuric acid giving an orange solution with a greenish fluorescence and is not precipitated back on dilution. It decomposes in contact with water and also when kept in moist air for a long time. (Found: C, 73.99; H, 3.85. $C_{19}H_{11}O_2Cl$ requires, C, 74.39; H, 3.58 per cent.).

The same compound was obtained by passing hydrogen chloride gas through a suspension of β -resorcyldieneacenaphthenone in dry ether. The experiment was conducted exactly in the same way as in the case of the corresponding salicylidene compound—only the hydrogen chloride gas was passed for a longer time (3 hours). The pyrylium chloride was purified as in the preceding case.

7-Hydroxy-2:3-acenaphthbenzopyrylium ferri-chloride.—It was prepared from the preceding compound in the same way as the corresponding ferri-chloride from 2:3-acenaphthbenzopyrylium chloride. The separated solid was purified by dissolving in a large excess of boiling acetic acid. On cooling, chocolate coloured needles separated. These were filtered, washed with ether, and dried. It decomposes at $236-37^{\circ}$. It is insoluble in almost all other organic solvents. It dissolves in concentrated sulphuric acid imparting to it a brownish colour with greenish fluorescence. (Found: C, 48.73; H, 2.44. $C_{19}H_{11}O_2$, $FeCl_4$ requires C, 48.64; H, 2.34 per cent.).

7-Hydroxy-2:3-Acenaphthbenzopyrylium perchlorate.—It was prepared and purified in a similar way and possessed properties similar to 2:3-acenaphthbenzopyrylium perchlorate (*vide supra*). It melts at 260° (decomp.) and burns with explosion. (Found: C, 61.27; 3.40. $C_{19}H_{12}O_6Cl$ requires C, 61.37; H, 3.23 per cent.).

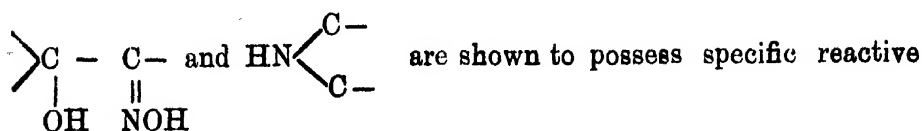
Review

Qualitative Analyse mit Hilfe von Tüpfel Reaktionen. (Qualitative Analysis with the help of 'spot' or 'drop' reactions) — By Dr. Fritz Feigl, University of Vienna. P. XII+387, with 12 figures in the text and 2 coloured plates. Published by Akademische Verlagsgesellschaft M.B.H. 1931, Leipzig. Stitched R.M. 26.40; bound R.M. 28.

Dr. Feigl, who is undoubtedly the pioneer in developing this branch of analytical micro-chemistry, which consists in testing substances in small drops of their solutions either on a filter paper or on a micro-crucible, is to be congratulated on bringing out this excellent book on the subject. The book, written by such an expert, will evidently commend itself to all analytical workers. The simplicity, rapidity and the minute quantities of substances, needed for identification, should render this method of analysis always preferable to the ordinary micro-methods for the economy of both time and material.

The book is divided mainly into two parts, theoretical and practical. The theoretical part opens with definition of the terms, sensitiveness, specificity, concentration limit and the minimum detectable limit (Erfassungsgrenze). A short but clear account of the theory of complex compounds has been added, as these latter play such an important part in the development of specific reactions. Chapters on the analytical use of the masking of reactions and the catalytic enhancement of reaction capacity of compounds furnish a very interesting study. Highly sensitive tests for phosphorus, arsenic and silicon by increasing the activity of molybdenum blue reaction through complex formation have been developed on the above basis. The application of iod-azid reaction, as an extremely sensitive and beautiful test for sulphide, polysulphide, thiocyanate and thio-sulphate, is another instance of the kind. The possibility of influencing the reactivity of a substance by means of induced reactions, and its analytical application have also been extensively discussed. Attempts have been made, with a fair degree of success, to classify the specific analytical activity of organic reagents as a result of the

presence of certain characteristic atomic groups. Thus, the groups



power for copper and silver respectively. The part played by capillarity, due to colloidal character of the filter paper, in performing the spot tests has also been emphasised.

In the practical part, after giving an account of the technique for carrying out the spot reactions, tests for individual metals and acids have been described in detail and the values for concentration limit and minimum detectable quantity have been given in each case. Methods have also been devised to detect a radicle in presence of others. Preparations of special organic reagents have been described wherever needed. Different methods for the systematic qualitative analysis of mixtures by spot reactions have been added towards the end. Finally, tests for traces of certain constituents in alloys, ores, stones, wood, leather etc., as well as the testing of purity of reagents have been described.

Both as a laboratory companion and as a reference book, it will prove to be of great service to all analytical chemists.

P. R.

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INDIAN CHEMICAL SOCIETY,

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XIV. Stereoisomeric Aminomethylenecamphors, Iminomethylenecamphors and their Derivatives.

BY BAWA KARTAR SINGH AND BRHUTNATH BHADURI.

For a comparative study of the effect of substitution on rotatory power of the derivatives of aminomethylenecamphor and iminomethylenecamphor, some of which have been already described (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1930, 7, 771; 1931, 8, 181; Singh, Bhaduri and Barat, *ibid.*, 1931, 8, 345), it is necessary to know the rotation constants of the parent compounds. With this object in view, the rotatory dispersion of stereoisomeric aminomethylenecamphors and iminomethylenecamphors have been described in the present paper.

The *laevo* and *racemic* isomerides of aminomethylenecamphors are new substances and were prepared in the usual way (*vide*, Experimental).

Benzylaminomethylenecamphors were prepared in the usual way by the condensation of benzylamine with oxymethylenecamphor (*d, l, dl*).

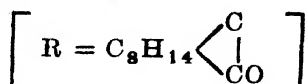
Iminomethylene-*d*-camphor was also prepared according to the method of Bishop, Claisen and Sinclair (*Annalen*, 1894, 281, 359), but the yield was very poor. It was, however, obtained in a better yield by the condensation of aminomethylene-*d*-camphor with oxymethylene-*d*-camphor (*vide*, Experimental). The *laevo*, *racemic* and the *meso* isomerides were prepared in the same way.

The Effect of Chemical Constitution and the Nature of Solvent on the Rotatory Power.

(i) On comparing the structural formulae and specific rotatory power of aminomethylenecamphor (I), anilinomethylenecamphor

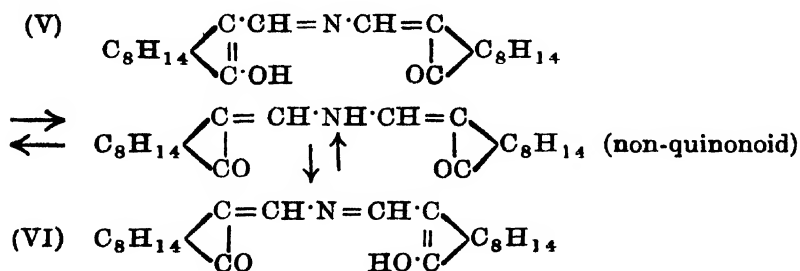
(II), and benzylaminomethylenecamphor (III), the following conclusions may be drawn:—

Structural formula.	$[\alpha]^{35^\circ}_{D_{5461}}$ (in chloroform).
I. $R=CH\cdot NH_2$	+350.0°
II. $R=CH\cdot NH\cdot C_6H_5$	424.6
III. $R=CH\cdot NH\cdot CH\cdot C_6H_5$	339.9
IV. $R=CH\cdot NH\cdot CH=R$	678.4



The phenyl group in (II) which is not in conjugation with the ethenoid and carbonyl groups has very little effect in increasing the rotatory power of the parent compound (I); and its further removal from the asymmetric centre by the interposition of the methylene group as in (III) lowers the rotation only to a slight extent (II→III).

(ii). The specific rotatory power of iminomethylenecamphor (IV), is nearly twice that of aminomethylenecamphor (I); this great increase in specific rotatory power can be accounted for by depicting the double symmetric tautomeric formula (V) for this compound, in which the conjugation between ethenoid, azethenoid and carbonyl groups is complete.



The compound does not, however, exhibit the expected fluorescence.

(iii) It is found that the order of decreasing rotatory power is ethyl alcohol > methyl alcohol > pyridine > acetone > chloroform > benzene, for aminomethylene-, and iminomethylenecamphors. The sequence of the dielectric constants of the solvents is also the same, except that the position of ethyl alcohol and methyl alcohol is reversed. The same is the case with pyridine and acetone in the above mentioned sequence. For iminomethylenecamphor, however,

the values of specific rotatory power in pyridine and acetone (Tables VIII and IX) become identical for Li_{6104} and beyond this towards the red end of the spectrum *e.g.*, Li_{6708} , that in acetone is greater than that for pyridine, whereas towards the violet region the order is reversed. For benzylaminomethylenecamphor, the order of decreasing rotatory power agrees exactly with the sequence of the dielectric constants of the solvents, *viz.*, methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene.

The Nature of Rotatory Dispersion.

* Optically active aminomethylenecamphors and iminomethylenecamphors, like their derivatives, obey the one-term simple dispersion formula of Drude, *viz.*, $[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$. On plotting $\frac{1}{[\alpha]}$ against λ^2 in each case a straight line is obtained. In the tables of rotatory dispersion (I—XI), a more exact test of the formula is provided by numerical calculations.

The value of the hypothetical absorption band in the ultra-violet region of the spectrum, λ_0 is lower for aminomethylenecamphor than that for iminomethylenecamphor, which shows that the absorption band is shifted towards the visible side of the spectrum in the case of the latter compound.

The Physical Identity of Isomers.

The values of rotatory power of *d* and *l* forms in different solvents (Tables I—XII) are identical within limits of experimental error. Out of 97 observations which are now recorded, in as many as 81 cases, the differences in the numerical value of the rotatory power of the opposite isomers correspond to a difference of less than 0.01° in the observed angle of rotation, and in other 15 cases, the corresponding angle lies between 0.01° to 0.02° , which is the limit of experimental error allowable in such measurements. Only in the remaining solitary case of iminomethylenecamphor in ethyl alcohol for Cd_{4800} (Table X), the difference corresponds to between 0.02° and 0.08° in the observed angle of rotation. This is, however, of the nature of casual experimental error. This, therefore, further supports Pasteur's principle of molecular dissymmetry, according to which the two forms, *dextro* and *laevo*, must possess equal and opposite rotatory power.

The melting point of the *racemic* form of aminomethylene-camphor is higher than that of the optically active isomers. This form is a true *dl*-compound, at least, in the solid state.

Examples of racemic forms having identical melting points with those of the active forms are very rare. A few examples have already been cited in a previous communication (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1931, 8, 623). In the present paper we record one more similar instance, *viz.*, iminomethylenecamphor (m. p. 216-18°).

EXPERIMENTAL.

Aminomethylene-d-camphor (I) was prepared in the same way as that of Bishop, Claisen and Sinclair (*loc. cit.*) and has the same crystalline form (shining white prisms), but melts at 157°, instead of 163-64°, which agrees with that observed by Rupe (*Helv. Chim. Acta*, 1920, 3, 50). (Found: C, 73·57; H, 9·73; N, 8·01. $C_{11}H_{17}ON$ requires C, 73·74; H, 9·50; N, 7·82 per cent.). The *l*-variety, m. p. 157°. (Found: N, 7·94). The *dl*-variety, m. p. 163-64°. (Found: N, 8·00).

Iminomethylene-d-camphor.—Aminomethylene-*d*-camphor (2·5 g.) dissolved in glacial acetic acid, was added to oxymethylene-*d*-camphor (2·5 g.) dissolved in methyl alcohol, and diluted with water when a precipitate separated at once. It was washed with dilute caustic soda solution and then with water and crystallised out of methyl alcohol as long needles, m. p. 216-18°, yield 80 p. c. It is freely soluble in chloroform and pyridine; less so in acetone and ethyl alcohol and difficultly soluble in methyl alcohol and benzene. (Found: C, 77·29; H, 9·15. $C_{22}H_{31}O_2N$ requires C, 77·42; H, 9·09; N, 4·11 per cent.). The *l*-variety, m. p. 216-18°. (Found: N, 4·20). The *dl*-variety, m. p. 216-18°. (Found: N, 4·29).

Iminomethylene-d-camphor was also prepared by the method of Bishop, Claisen and Sinclair (*loc. cit.*) by the action of strong hydrochloric acid on aminomethylene-*d*-camphor. The yield is, however, very poor, but the melting point is the same as by the above mentioned method. The mixed melting point of the product prepared by the two methods was also 216-18°. Bishop, Claisen and Sinclair (*loc. cit.*) give 221-22° as the melting point.

Internally Compensated or meso-Iminomethylenecamphors.—(1) Aminomethylene-*d*-camphor (1 mol.) in glacial acetic acid was added to oxymethylene-*l*-camphor (1 mol.) and the precipitate so obtained was repeatedly crystallised out of dilute methyl alcohol

as white prismatic needles, m. p. 217-18°. (Found: C, 77.25; H, 9.17. $C_{22}H_{31}O_2N$ requires C, 77.42; H, 9.09; N, 4.11 per cent.).

(2) In the same way amidomethylene-*l*-camphor was condensed with oxymethylene-*d*-camphor and white prismatic needles melting at 217-18° were obtained. (Found: N, 4.23).

On polarimetric examination both the compounds were found to be inactive.

The condensed product of oxymethylenecamphor with methylamine (obtained in the usual way) was an oil which refused to solidify.

Benzylaminomethylene-d-camphor (III).—Oxymethylene-*d*-camphor was condensed in the usual way with benzylamine hydrochloride in presence of a little fused sodium acetate and the oil obtained on dilution with water was left overnight when it solidified. It was crystallised out of dilute methyl alcohol (charcoal) as fine white needles, m. p. 89-91°. It is freely soluble in all the ordinary organic media. (Found: C, 80.18; H, 8.70; N, 5.41. $C_{18}H_{23}ON$ requires C, 80.30; H, 8.55; N, 5.21 per cent.). The solutions of the substance in different solvents (except in ethyl alcohol, Table XI) exhibited rapid mutarotation and turned scarlet in a short time; hence their rotatory dispersion could not be studied for more than two lines (Table XII). The *l*-form, m.p. 89-91°. (Found: N, 5.36). The *dl*-form, m.p. 84-85°. (Found: N, 5.40).

The rotatory power determinations were made in a 2-dm jacketed tube at 35°. The value of λ_0 , calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

TABLE I.

Aminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{68.33}{\lambda^2 - 0.1025} ; \lambda_0 = 0.3202.$$

conc. g/100 c.c.	Dextro		Line.	calc. $[\alpha]$ c.	Laevo		
	obs. $[\alpha]$ o	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4000	+535.0°	+0.3°	Cd ₄₈₀₀	±534.7°	-1.2°	-533.5°	0.4040
	436.3	-1.1	Cd ₅₀₈₆	437.4	+0.7	438.1	
	403.8	-1.0	Ag ₅₃₀₉	404.8	± 0	404.8	
	350.0	+0.9	Hg ₅₄₆₁	349.1	-0.2	348.9	
	296.8	+1.2	Hg ₅₇₈₀	295.1	+0.6	295.7	
	278.8	-0.5	Na ₅₈₉₃	279.3	-0.1	279.2	
	258.8	+0.8	Li ₆₁₀₄	253.0	+0.7	253.7	
	218.8	-0.2	Cd ₆₄₃₈	219.0	+0.1	219.1	
	196.8	-0.3	Li ₆₇₈₈	196.6	-1.0	195.6	

The solution exhibited slight mutarotation; the initial values $[\alpha]_{\text{Hg5461}} = 350.0^\circ$ and $[\alpha]_{\text{Hg5780}} = 296.3^\circ$ changing to 345.0° and 290.0° respectively in course of 20 hours.

TABLE II.

Aminomethylenecamphor in Acetone.

$$[\alpha] = \pm \frac{72.04}{\lambda^2 - 0.0944} ; \lambda_0 = 0.3072.$$

<i>Dextro</i>			Line.	calc. $[\alpha]$ c.	<i>Laevo</i>		
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4036	+438.6°	+0.1°	Cd ₅₀₈₆	±438.5°	-1.0°	-437.5°	0.4000
	406.5	-0.8	Ag ₅₃₀₉	407.3	+0.2	407.5	
	354.3	+0.8	Hg ₅₄₆₁	353.5	+0.3	353.8	
	301.1	+0.6	Hg ₅₇₈₀	300.5	-0.5	300.0	
	283.7	-1.3	Na ₅₈₉₃	285.0	± 0	285.0	
	259.0	+0.1	Li ₆₁₀₄	258.9	-0.1	258.8	
	224.3	-0.8	Cd ₆₄₃₈	225.1	-0.1	225.0	
	202.0	-0.6	Li ₆₇₀₈	202.6	-0.1	202.5	

The solution did not exhibit mutarotation.

TABLE III.

Aminomethylenecamphor in Methyl Alcohol.

$$[\alpha] = \pm \frac{75.33}{\lambda^2 - 0.1919} ; \lambda_0 = 0.3192.$$

<i>Dextro</i>			Line.	calc. $[\alpha]$ c.	<i>Laevo</i>		
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4004	+479.6°	+1.1°	Cd ₅₀₈₆	±478.5°	-0.5°	-478.0°	0.4048
	442.1	-0.8	Ag ₅₃₀₉	442.9	+0.5	443.4	
	383.4	+1.2	Hg ₅₄₆₁	382.2	-0.5	381.7	
	323.4	+0.3	Hg ₅₇₈₀	323.1	+0.5	323.6	
	304.7	-1.1	Na ₅₈₉₃	305.8	-0.7	305.1	
	277.3	+0.2	Li ₆₁₀₄	277.1	+0.8	277.9	
	239.6	-0.2	Cd ₆₄₃₈	240.0	-0.4	239.6	
	214.9	-0.6	Li ₆₇₀₈	215.5	+0.7	216.2	

The solution exhibited mutarotation; the initial values $[\alpha]_{\text{Hg5461}} = 383.4^\circ$ and $[\alpha]_{\text{Hg5780}} = 323.4^\circ$ changing to 368.4° and 308.4° respectively in course of 20 hours.

TABLE IV.

Aminomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{77.13}{\lambda^2 - 0.1006} ; \quad \lambda_0 = 0.3172.$$

<i>Dextro</i>			Line.	<i>Laevo</i>			
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.		calc. $[\alpha]$ c.	o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.3996	+486.7°	-1.2°	Cd ₅₀₈₆	+487.9°	+0.9°	-486.8°	0.4040
	451.7	-0.2	Ag ₅₂₀₉	451.9	-0.1	451.8	
	390.3	± 0	Hg ₅₄₆₁	390.3	-0.4	399.9	
	830.4	+0.1	Hg ₅₇₈₀	330.3	+0.3	330.6	
	312.7	-0.1	Na ₅₈₉₃	312.8	+0.3	313.1	
	284.2	+0.7	Li ₆₁₀₄	283.5	-0.1	283.4	
	246.5	+0.8	Cd ₆₄₃₈	245.7	-0.6	245.1	
	220.3	-0.4	Li ₆₇₀₈	220.7	+0.8	221.5	

The solution exhibited mutarotation; the initial values $[\alpha]_{\text{Hg}_{5461}} = 390.3^\circ$ and $[\alpha]_{\text{Hg}_{5780}} = 330.4^\circ$ changing to 367.9° and 306.6° respectively in course of 20 hours.

TABLE V.

Aminomethylenecamphor in Benzene.

$$[\alpha] = \pm \frac{74.90}{\lambda^2 - 0.0816} ; \quad \lambda_0 = 0.2857.$$

<i>Dextro</i>			Line.	<i>Laevo</i>			
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.		calc. $[\alpha]$ o.	o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.3996	+422.8°	-0.2°	Cd ₅₀₈₆	+423.0°	+1.0°	-424.0°	0.4080
	394.2	-0.6	Ag ₅₂₀₉	394.8	-0.1	394.7	
	346.6	+0.7	Hg ₅₄₆₁	345.9	-0.3	345.6	
	297.7	+1.1	Hg ₅₇₈₀	296.6	± 0	296.6	
	281.5	-0.4	Na ₅₈₉₃	281.9	± 0	281.9	
	257.8	+0.4	Li ₆₁₀₄	257.4	-0.1	257.3	
	225.2	+0.2	Cd ₆₄₃₈	225.0	+0.5	225.5	
	202.7	-0.6	Li ₆₇₀₈	203.3	+0.2	203.5	

The solution exhibited mutarotation; the initial values $[\alpha]_{\text{Hg}_{5461}} = 346.6^\circ$ and $[\alpha]_{\text{Hg}_{5780}} = 297.7^\circ$ changing to 336.6° and 287.7° respectively in course of 8 hours.

TABLE VI.

Aminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{79.94}{\lambda^2 - 0.0898} ; \quad \lambda_0 = 0.1120.$$

<i>Dextro</i>			Line.	<i>Laevo</i>			
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.		calc. $[\alpha]$ o.	o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
3.0016	+471.7°	-0.1°	Cd ₅₀₈₆	±471.8°	+0.2°	-472.0°	3.0024
	438.9	-0.2	Ag ₅₂₀₉	439.1	-0.3	438.8	
	382.4	-0.1	Hg ₅₄₆₁	382.5	±0	382.5	
	326.15	-0.35	Hg ₅₇₈₀	326.5	-0.3	326.2	
	309.9	+0.1	Na ₅₈₉₃	309.8	-0.3	309.5	
	282.1	±0	Li ₆₁₀₄	282.1	+0.1	282.2	
	245.5	-0.1	Cd ₆₄₃₈	245.6	±0	245.6	
	221.9	+0.3	Li ₆₇₀₈	221.6	+0.25	221.85	

The solution did not exhibit any mutarotation.

TABLE VII.

Iminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{124.9}{\lambda^2 - 0.1139} ; \quad \lambda_0 = 0.3875.$$

<i>Dextro</i>			Line.	<i>Laevo</i>			
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.		calc. $[\alpha]$ c.	o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4032	+1072.0°	-1.0°	Cd ₄₈₀₀	±1073.0°	-0.5°	-1072.5°	0.4000
	862.0	-0.6	Cd ₅₀₈₆	862.6	-0.1	862.5	
	792.5	-1.1	Ag ₅₂₀₉	793.6	+0.2	793.8	
	678.4	-0.6	Hg ₅₄₆₁	677.8	-0.3	677.5	
	568.1	±0.8	Hg ₅₇₈₀	567.3	+0.2	567.5	
	535.8	+0.6	Na ₅₈₉₃	535.2	-0.2	535.0	
	482.4	-0.4	Li ₆₁₀₄	482.8	+1.0	482.8	
	415.5	±0	Cd ₆₄₃₈	415.5	+0.8	416.3	
	372.1	+0.4	Li ₆₇₀₈	371.7	-0.4	371.8	

The solution did not exhibit mutarotation.

TABLE VIII.

Iminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{122.4}{\lambda^2 - 0.1291} ; \quad \lambda_0 = 0.8593.$$

<i>Dextro</i>			Line.	calc. $[\alpha]$ c.	<i>Laevo</i>		
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4000	+1206.3°	-1.7°	Cd ₄₈₀₀	±1208.0	+0.4°	-1208.4°	0.4072
	945.0	+0.5	Cd ₅₀₈₆	944.5	-0.2	944.3	
	861.3	+0.5	Ag ₅₂₀₉	860.8	-1.0	859.8	
	722.5	-1.3	Hg ₅₄₆₁	723.8	-0.6	723.2	
	596.3	-0.7	Hg ₅₇₈₀	597.0	+1.0	598.0	
	561.3	+0.4	Na ₅₈₉₃	560.9	+0.4	561.3	
	508.8	+1.1	Li ₆₁₀₄	502.7	-0.4	502.3	
	428.8	-0.1	Cd ₆₄₃₈	428.9	-0.3	428.6	
	381.3	-0.1	Li ₆₇₀₈	381.4	+0.6	382.0	

The solution did not exhibit mutarotation.

TABLE IX.

Iminomethylenecamphor in Acetone.

$$[\alpha] = \pm \frac{127.4}{\lambda^2 - 0.1194} ; \quad \lambda_0 = 0.8455.$$

<i>Dextro</i>			Line.	calc. $[\alpha]$ c.	<i>Laevo</i>		
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4000	+1146.3°	-1.7°	Cd ₄₈₀₀	±1148.0°	-1.0°	-1147.0°	0.4060
	913.8	-0.5	Cd ₅₀₈₆	914.3	-0.4	913.9	
	838.8	+0.1	Ag ₅₂₀₉	838.7	+0.2	838.9	
	713.7	+1.3	Hg ₅₄₆₁	712.4	-0.4	712.0	
	592.5	-0.8	Hg ₅₇₈₀	593.3	+0.4	593.7	
	560.0	+1.2	Na ₅₈₉₃	558.3	-0.8	558.0	
	508.8	+0.8	Li ₆₁₀₄	503.0	-0.4	502.6	
	431.3	-0.3	Cd ₆₄₃₈	431.6	+0.7	432.3	
	385.0	-0.2	Li ₆₇₀₈	385.2	+0.3	385.5	

The solution did not exhibit any mutarotation.

TABLE X.

Iminomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{100 \alpha}{\lambda^2 - 0.1245}; \quad \lambda_0 = 0.3528.$$

<i>Dextro</i>			Line.	<i>Laevo</i>			
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.		calc. $[\alpha]$ c.	o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.3992	+1252.6°	+1.6°	Cd ₄₈₀₀	±1251.0°	-1.0°	-1250.0°	0.4040
	986.0	-0.7	Cd ₅₀₈₆	986.7	+0.9	987.6	
	901.8	-0.8	Ag ₅₃₀₉	902.6	+0.8	903.4	
	761.7	-0.7	Hg ₅₄₆₁	762.4	+0.1	62.5	
	632.6	+0.8	Hg ₅₇₈₀	631.8	-0.5	631.3	
	593.8	-0.6	Na ₅₈₉₃	594.4	-0.4	594.0	
	533.6	-0.1	Li ₆₁₀₄	533.7	-0.2	533.5	
	457.1	+0.1	Cd ₆₄₃₈	456.7	+0.1	456.8	
	407.1	+0.3	Li ₆₇₀₈	406.8	+0.5	407.3	

The solution did not exhibit any mutarotation.

TABLE XI.

Benzylaminomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{65.77}{\lambda^2 - 0.1112}; \quad \lambda_0 = 0.3335.$$

<i>Dextro</i>			Line.	calc. $[\alpha]$ c.	<i>Laevo</i>		
conc. g/100 c.c.	obs. $[\alpha]$ o.	o-c.			o'-c.	obs. $[\alpha]$ o'.	conc. g/100 c.c.
0.4020	+352.0°	+0.3°	Hg ₅₄₆₁	±351.7°	-0.1°	-351.6°	0.4052
	294.8	-0.2	Hg ₅₇₈₀	295.0	-0.1	294.9	
	278.7	+0.1	Na ₅₈₉₃	278.6	+0.3	278.9	
	251.3	-0.3	Li ₆₁₀₄	251.6	+0.1	251.7	
	217.7	+0.7	Cd ₆₄₃₈	217.0	+0.2	217.2	
	193.1	-1.0	Li ₆₇₀₄	194.1	-0.4	193.7	

The solution exhibited mutarotation; the initial values $[\alpha]_{\text{Hg}_{5461}} = 352.0^\circ$ and $[\alpha]_{\text{Hg}_{5780}} = 294.8^\circ$ changing to 340.7° and 284.8° respectively in course of 4 hours.

TABLE XII.

Benzylaminomethylenecamphor.

solvent.	conc. g/100 c.c.	<i>d</i> or <i>l</i> .	Hg ₅₄₆₁ .	Hg ₅₇₈₀ .
Chloroform	0·4032	<i>d</i>	+ 339·9°	+ 279·1°
	0·4000	<i>l</i>	- 340·0	- 278·8
Methyl alcohol	0·4020	<i>d</i>	+ 365·7	+ 307·3
	0·4060	<i>l</i>	- 364·6	- 307·9
Benzene	0·4052	<i>d</i>	+ 297·4	+ 245·6
	0·4004	<i>l</i>	- 297·2	• - 244·8

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Condensation of Butylchloral with Gallic Acid and the Three Cresotic Acids.

By (Miss) B. N. KATRAK AND A. N. MELDRUM.

The study of the condensation of butylchloral, $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CHO}$ with hydroxy- and methoxybenzoic acids was undertaken in order to compare its behaviour in sulphuric acid condensations with that of chloral.

The condensation of chloral with methoxybenzoic acid has been studied by Fritsch (*Annalen*, 1897, **296**, 358; 1898, **301**, 360), Meldrum (*J. Chem. Soc.*, 1911, **99**, 1712), Bargellini and Molina (*Atti R. Accad. Lincei*, 1912, **21**, II, 146) and by Alimchandani and Meldrum (*J. Chem. Soc.*, 1920, **117**, 964); the last mentioned extending their researches to the condensation of chloral with hydroxybenzoic acids (*J. Chem. Soc.*, 1921, **119**, 201).

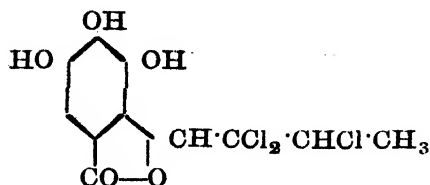
The general method adopted throughout this work was to dissolve equimolecular amounts of the two substances in sulphuric acid and after twenty four hours to pour the mixture on to ice.

Equimolecular amounts of gallic acid and butylchloral hydrate yielded 8:4:5-trihydroxy-2- $\alpha\alpha\beta$ -trichloropropyl phthalide (I) which corresponds to and reacts in the same manner as the chloral product. It gives a triacetyl compound and the solution in sodium hydroxide turns dark brown in air.

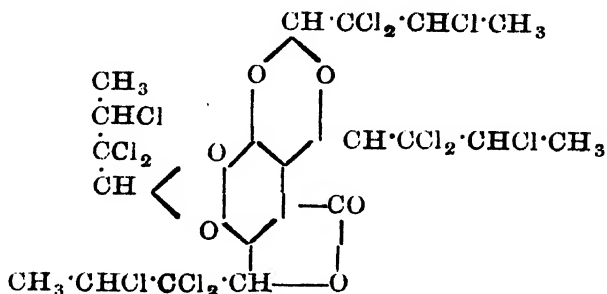
With excess (2 mols.) of butylchloral, (I) is again obtained mixed with (II) which contains four butylchloral groups and which, if Meldrum and Alimchandani's views for the chloral compound (*loc. cit.*) be adopted, can be regarded as containing heterocyclic rings. This compound is insoluble in concentrated sulphuric acid and sodium hydroxide solution, and does not form an acetyl derivative.

The trimethoxy derivative of (I) was difficult to prepare by direct methylation; it was obtained by condensing trimethoxybenzoic acid with butylchloral. For this purpose, 85 p.c. sulphuric

acid was found most suitable; with sulphuric acid of higher concentrations, mixtures of di- and trimethoxy derivatives were obtained. In the corresponding reaction with chloral the dimethoxy derivative only was isolated.



(I)



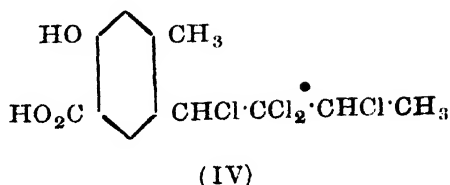
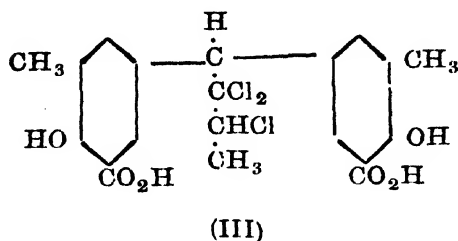
(II)

Both the triacetyl- and the trimethoxyphthalides, when reduced with zinc dust and acetic acid give the respective *monochloro* compounds, containing the group $\text{CH} \cdot \text{CCl} : \text{CH} \cdot \text{CH}_3$.

The reduced trimethoxy compound is very stable. It dissolves slowly in caustic soda solution on boiling without change of colour and the original substance is reprecipitated on acidification. It may be assumed that the phthalide ring is opened by alkali and is again closed on acidification. On treatment with sulphuric acid (conc.), the reduction product was not affected.

In the first experiments on the condensation of butylchloral with the three cresotic acids, *diacidic* compounds were obtained; (III) was obtained from the *o*-acid. Meldrum and Alimchandanji (*loc. cit.*) isolated a similar compound from the interaction of the acid and chloral. The behaviour of the *p*-acid is thus different from

its behaviour towards chloral with which it gives a heterocyclic ring.



In order to get a simple (1:1) compound, the method was so modified as to yield a slow and continuous current of hydrogen chloride. In this way the *m*-acid yielded easily the compound (IV). It is assumed, in line with Alimchandani and Meldrum's results, that substitution occurs in the *p*-position to the hydroxyl group. From the *o*- and *p*-acids similar compounds were obtained by using excess of butylchloral (2 mols.) and heating the mixture.

EXPERIMENTAL.

3:4:5-Trihydroxy-2- $\alpha\beta$ -trichloropropyl phthalide, (I).—Gallic acid (17 g.) and butylchloral hydrate (19 g.) were dissolved in sulphuric acid (95 p.c.). After 24 hours, the mixture was poured on to ice. The product separated as a spongy mass which slowly became crystalline. It crystallised from acetic acid in colourless prisms, m.p. 260°. (Found: Cl, 32.7. $C_{11}H_9O_5Cl_3$ requires Cl, 32.5 per cent.).

The acetyl derivative crystallises in long needles from methyl alcohol, m.p. 161.62°. (Found: Cl, 23.7. $C_{17}H_{15}O_8Cl_3$ requires Cl, 23.4 per cent.).

Compound (II).—Gallic acid (8.5 g.), butylchloral hydrate (19 g.) and sulphuric acid (100 c.c. 95 p.c.) gave after 24 hours

a white solid. Cold alkali does not dissolve it but changes its colour probably due to decomposition. It crystallises from chloroform in beautiful clusters of needles, m.p. 281-82°. (Found: Cl, 51.7. $C_{23}H_{20}O_6Cl_{12}$ requires Cl, 52.1 per cent.).

3:4:5-Trimethoxy-2- $\alpha\beta$ -trichloropropyl phthalide was prepared by condensing trimethylgallic acid with butyl chloralhydrate. Sulphuric acid of 85 p. c. concentration was found most suitable. With a lower concentration (75 p.c.) the condensation did not proceed at all. With sulphuric acid of 90 p. c. and 100 p. c. concentrations a spongy mass was obtained. It was resolved by successive crystallisation from several organic solvents into syringic acid, its condensation product, (*vide infra*) and the trimethoxy condensation product.

Trimethyl gallic acid (21 g.) and butylchloral hydrate (19 g.) were dissolved in sulphuric acid (85 p.c. 62 c.c.) and the mixture after 10 days, was poured on to ice when a semi-solid mass separated which crystallised from methyl alcohol in transparent plates, m. p. 90-91°. From the methyl alcoholic mother liquor syringic acid and its condensation product were obtained.

3:4:5-Trimethoxy- and 3:4:5-triacetyl-2- α -chloro- α -propylene phthalides were prepared by reducing the corresponding tri-derivatives with Zn dust and acetic acid. It was necessary to warm the mixtures from time to time. Both products were recrystallised from acetone and petroleum ether for analysis.

The trimethoxy compound melts at 110-11°. (Found: Cl, 12.2. $C_{14}H_{15}O_5Cl$ requires Cl, 11.9 per cent.). The triacetyl compound melts at 145°. (Found: Cl, 9.5. $C_{17}H_{15}O_8Cl$ requires Cl, 9.3 per cent.).

The trimethoxy compound dissolves in sodium hydroxide solution (N/10) on boiling, and the original substance is reprecipitated on acidification. Cold sulphuric acid (conc.) dissolves the substance without evolution of HCl gas even on warming and the original substance is obtained on diluting the acid solution. The triacetyl derivative is not so stable.

4-Hydroxy - 3:5-dimethoxy-2- $\alpha\beta$ -trichloropropyl phthalide.—Syringic acid (15 g.), butylchloral hydrate (15 g.) and sulphuric acid (95 p.c. 90 c.c.) were mixed and after 10 days, during which the mixture was warmed from time to time, it was poured on to ice. The solid, separating, was crystallised from benzene and petroleum ether, m. p. 154-55°. (Found: Cl, 30.2. $C_{13}H_{13}O_5Cl_3$ requires Cl, 29.9 per cent.).

The *acetyl derivative* crystallises from absolute alcohol in transparent needles, *m. p.* 169-70°. (Found: Cl, 27.1. $C_{15}H_{15}O_6Cl_3$ requires Cl, 26.8 per cent.).

$\alpha\alpha\beta$ - *Trichloro-di (3-methyl-4-hydroxy-5-carboxyphenyl) - butane*, (III).—*o*-Cresotic acid (4 g.), butylchloral hydrate (5 g.) and sulphuric acid (sufficient to form a solution) were mixed; after 24 hours the mixture was poured on to ice. The product (III) was crystallised from acetic acid, *m. p.* 289°. (Found: Cl, 23.0. $C_{20}H_{19}O_6Cl_3$ requires Cl, 23.1 per cent.).

The corresponding *p*- and *m*-compounds were similarly prepared from the respective acids. The *p*-product was crystallised from nitrobenzene and then from acetone and toluene, *m. p.* 277°. (Found: Cl, 23.3 p.c.). The *m*-product was crystallised from xylene and then from acetic acid in transparent plates, *m. p.* 298°. (Found: Cl, 23.2 per cent.).

1- $\alpha\beta\beta\beta$ -*Tetrachlorobutyl-2-methylhydroxy-5-benzoic acid*, (IV).—*m*-Cresotic acid (4 g.), butylchloral hydrate (5 g.) and a little coarse sodium chloride were dissolved in sulphuric acid (95 p.c.). More sodium chloride and sulphuric acid were added at intervals. After 24 hours, the mixture was poured on to ice. The product was crystallised from toluene in clusters of needles, *m. p.* 210°. (Found: Cl, 40.9. $C_{12}H_{12}O_3Cl_4$ requires Cl, 41.0 per cent.).

The corresponding *p*- and *o*-compounds required an excess of butylchloral (2 mols.) and heat. For the former, occasional warming was sufficient, but the preparation of the latter involved heating to 50-60° for 3 days.

The *p*-compound crystallised from benzene in clusters of needles, *m. p.* 211-12°. (Found: Cl, 40.9 p.c.). The *o*-compound was crystallised from toluene, *m. p.* 204-05°. (Found: Cl, 40.6 p.c.).

The *o*-acid has a strong tendency to form the diacidic compound, which rendered purification difficult.

3- $\alpha\beta\beta\beta$ -*Tetrachloroethyl-5-methyl-6-hydroxybenzoic acid*.—This modified method was also tried with *o*-cresotic acid (1 mol.) chloral hydrate (3 mols.) and sodium chloride and sulphuric acid as before. After 2 days, the mixture was poured on to ice and the product crystallised from carbon tetrachloride, *m. p.* 184-85°. (Found: Cl, 44.8. $C_{10}H_8O_3Cl_4$ requires Cl, 44.6 per cent.).

A Study of the Interaction between Thionyl Chloride and Substances containing the Reactive Methylene (-CH₂-) Group. Part III.

BY K. G. NAIK AND V. B. THOSAR.

The present work is a direct continuation of a previous work (Naik and Parekh, *J. Indian Chem. Soc.*, 1930, 7, 137) the amides used being the substituted amides of acetoacetic acid and acetone dicarboxylic acid. The aim of this work is to show that the reactivity of the hydrogen atoms of the reactive methylene (-CH₂-) group, situated between two carbonyl groups, with respect to thionyl chloride, is in complete accordance with the hypothesis put forward (Naik, *J. Chem. Soc.*, 1921, 119, 1166, 1231; Naik and Avasare, *J. Chem. Soc.*, 1922, 121, 2592), *viz.*, that the interaction of sulphur monochloride and a compound containing a reactive methylene group, depends upon the nature of the groups attached to the two remaining valencies of the carbon atom.

Thionyl chloride was made to react with following amides in presence of dry benzene.

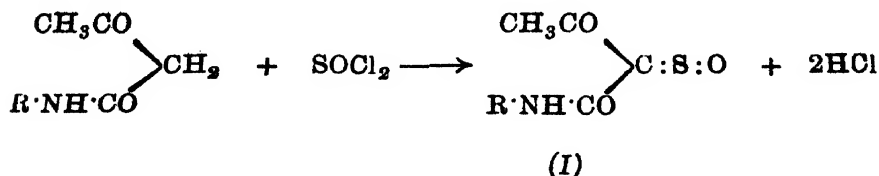
(1) Acetoacetanilide, (2) acetoacet-*o*-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet-*p*-toluidide, (5) acetoacet- α -naphthylamide, (6) acetoacet- β -naphthylamide, (7) acetoacet-(1:3:4)-xylidide, (8) acetoacet-(1:4:5)-xylidide, (9) acetone dicarboxyanilide, (10) acetone dicarboxy-*o*-toluidide, (11) acetone dicarboxy-*p*-toluidide, (12) acetone dicarboxy- α -naphthylamide and (13) acetone dicarboxy- β -naphthylamide.

When the solution was refluxed there was a copious evolution of hydrochloric acid with a change in the colour of the solution. The reaction was complete at the end of one hour.

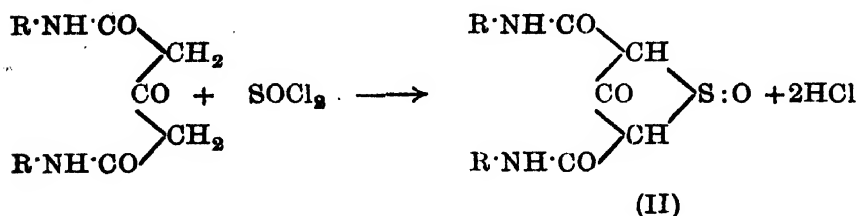
The preparation of the substituted amides of acetoacetic acid was first attempted following the method described by Knorr (*Annalen*, 1896, 236, 75) which was subsequently discarded, yield being found extremely unsatisfactory. After some trials, the method used by Ewins and King (*J. Chem. Soc.*, 1913, 103, 104) with some modifications was found to yield satisfactory results. For the preparation of the substituted amides of acetone dicarboxylic acid, the method

described by Bésthorn and Garben (*Ber.*, 1900, 33, 3439) was adopted. Amides (5 to 8) and (12 to 13) have been prepared for the first time.

The reaction in the case of substituted amides of acetoacetic acid (1 to 8) can be represented thus:



In the case of the substituted amides of acetone dicarboxylic acid (9 to 13), although more than two molecules of thionyl chloride were taken for every molecule of the substituted amide to give ample opportunity for the substitution of sulphoxide groups for all the hydrogen atoms in the two reactive methylene groups, reaction did not proceed to this extent and the product contained only one sulphoxide group, one hydrogen atom of each methylene group having been substituted.



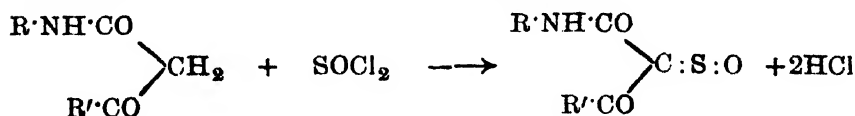
The above constitution of the sulphur compounds follows from the following considerations:

(i) That the two hydrogen atoms are not supplied by the phenyl group follows from the reasons, (a) malondimethyl amide which does not contain such a phenyl nucleus reacts similarly with thionyl chloride to give a similar sulphoxide (Naik and Parekh, *loc. cit.*); (b) acetone dicarboxyanilide which contains two such phenyl groups also gives the same type of compound. On the supposition that the phenyl group is reactive, such a compound cannot be expected.

(ii) That the two hydrogen atoms are not those which are originally attached to the nitrogen atom of the $\text{-NH}\cdot\text{R}$ group for, (a) in the first place there is only one such hydrogen in a molecule of acetoacetanilide, while two hydrogen atoms have taken part in the reaction from the same molecule of acetoacetanilide; (b) a tertiary

amide like malondimethylphenylamide which does not contain such amido hydrogen, reacts under similar conditions with thionyl chloride to give a similar compound (Naik and Parekh, *loc. cit.*).

Now taking into considerations the three compounds (i) $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{R}$, (ii) $\text{R} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{R}$ and (iii) $\text{R} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{R}$ it will be seen that the total negativity of the carbonyl groups with their attached radicles in the case of (i) is due to two groups, one of which $-\text{CO} \cdot \text{NH} \cdot \text{R}$ is common to all the three compounds and the other, the acetyl group, which is more negative than the partly neutralised group $-\text{CO} \cdot \text{NH} \cdot \text{R}$ which is present in (ii) and (iii). Again, the negative effect of the central carbonyl group in (iii) is divided between two adjacent methylene groups, so that the total negative effect on each of the methylene group is smaller than that on a single methylene group when linked as $-\text{CO} \cdot \text{CH}_2 \cdot \text{CO}-$ as in (i) or (ii). Hence it was expected that the two methylene groups in (iii) would be less reactive than the one in (ii), which in its turn would be less reactive than that in (i). From the facts stated above, it will be quite evident that such has actually been found to be the case. Whereas compounds of the type (iii) have given rise to sulphoxides of the type (II), compounds of the type (ii) and (i) reacted thus :



where R' is $-\text{CH}_3$ or $-\text{NH} \cdot \text{R}$ group. Reaction in the case of (i) however is much faster than in case (ii). Such behaviour is quite in accordance with the theory, already referred to above.

As compared with the sulphoxides of the substituted amides of malonic acid, these sulphoxides are not degraded into sulphides by boiling in benzene solution in presence of a catalyst like thionyl chloride, hydrochloric acid gas or iodine. They are also more stable towards moisture.

EXPERIMENTAL.

Acetoacet- α -naphthylamide.—Acetoacetic ester (13 g.) was mixed with α -naphthylamine (14 g.) in a conical flask with an air condenser, and the mixture was heated quickly to boiling and kept gently boiling for $1\frac{1}{2}$ minutes. On cooling, the amide crystallised out. It was filtered and washed with a mixture of benzene and light petroleum (1:1)

till it was free from the ester and the amine. It was then redissolved in hot benzene and filtered from the insoluble residue of the diamide which was also formed in the course of reaction. The filtrate was diluted with an equal volume of light petroleum (b.p. 50-60°) and allowed to cool. Acetoacet- α -naphthylamide crystallised out in pale red small needles, m.p. 108-09°. It is highly soluble in ethyl alcohol, methyl alcohol, benzene and nearly insoluble in light petroleum. (Found: N, 6.12. $C_{14}H_{13}O_2N$ requires N, 6.16 per cent.).

Rest of the substituted amides of acetoacetic acid (6 to 8) were similarly prepared by condensing the respective amines with ethyl acetoacetate. The results are tabulated in Table I.

Acetone dicarboxy- α -naphthylamide.—Acetone dicarboxylic ester (10 g.) and α -naphthylamine (11 g.) were mixed together and heated in a sealed tube at 130° for 24 hours. The reaction mixture was diluted with about 500 c.c. of benzene when the amide separated out. It was filtered and washed with benzene till free from ester and finally with ether to remove amine. It was then recrystallised from hot alcohol as pale red granular mass, m.p. 165°. It is fairly soluble in glacial acetic acid, sparingly so in alcohol but insoluble in benzene, toluene, light petroleum or ether. (Found: N, 6.94. $C_{23}H_{20}O_3N_2$ requires N, 7.07 per cent.).

Acetone dicarboxy- β -naphthylamide was similarly prepared from acetone dicarboxylic ester and β -naphthylamine. The results are tabulated in Table II.

Acetoacetanilide sulphoxide.—Pure dry acetoacetanilide (1.7 g.) was made to react with thionyl chloride (1.4 g.) in presence of dry benzene (30 c.c.). After refluxing for 1 hour, when the evolution of hydrochloric acid had nearly ceased, the clear solution obtained was concentrated and allowed to cool. Nothing separated out. Hence it was slowly added to a large amount of dry light petroleum (b.p. 50-60°) when a beautiful snuff coloured compound separated out. It was redissolved in benzene and separated by slow addition of light petroleum. It was then kept in an alkali desiccator till it was free from hydrochloric acid. It melts with decomposition to a thick black liquid at 90°, with a previous shrinking at 69°. (Found: N, 6.43; S, 14.26. $C_{10}H_9O_3NS$ requires N, 6.27; S, 14.35 per cent.).

All other sulphoxides were similarly prepared by treating the respective amides (1 mol.) with thionyl chloride (1 mol.) under similar conditions. The results are tabulated in Table III.

TABLE I.

New Substituted Amides of Acetoacetic Acid.

Name.	Formula.	Appearance.	Duration of heating.	M.p.	Analysis.	
					Found.	Calc.
Acetoacet- α naphthylamide	$C_{14}H_{13}O_2N$	Pale red short needles.	$1\frac{1}{2}$ min.	108-109°	N, 6.12	6.16 p.c.
Acetoacet- β naphthylamide	$C_{14}H_{13}O_2N$	White crystals.	$1\frac{1}{2}$	103-104°	N, 6.57	6.16
Acetoacet-(1:3:4)-xylidide	$C_{13}H_{15}O_2N$	White short needles.	$1\frac{1}{2}$	92°	N, 7.12	6.82
Acetoacet-(1:4:5)-xylidide	$C_{13}H_{15}O_2N$	Shining white tufts.	$1\frac{1}{2}$	96°	N, 6.95	6.82

TABLE II.

New Substituted Amides of Acetone dicarboxylic Acid.

Acetone dicarboxy- α -naphthylamide	$C_{25}H_{20}O_3N_2$	Pale red granular mass.	24 hrs.	165°	N, 6.94	7.07
Acetone dicarboxy- β -naphthylamide	$C_{25}H_{20}O_3N_2$	White needles.	24	207°	N, 6.71	7.07

TABLE III.

Condensation Products of Thionyl Chloride with Substituted Amides of Acetoacetic and Acetone dicarboxylic Acids.

(S = Sulphoxide).

Name.	Formula.	Appearance.	Shrinks at.	M.p. (with decomp.).	Analysis	
					Found.	Calc.
Acetosacetanilide-S	$C_{10}H_9O_3NS$	Snuff colour	69°	90°	S, 14.26 N, 6.43	14.35 p.c. 6.37
Acetosacet-o-toluidide-S	$C_{11}H_{11}O_3NS$	Pale brown	87°	110°	S, 13.79 N, 5.94	13.50 5.90
Acetosacet-m-toluidide-S	$C_{11}H_{11}O_3NS$	"	78°	98-94°	S, 13.70	13.50
Acetosacet-p-toluidide-S	$C_{11}H_{11}O_3NS$	Deep brown	87°	92-93°	S, 13.17	13.50
Acetosacet- α -naphthylamide-S	$C_{14}H_{11}O_3NS$	Pale brown	92°	112°	S, 11.34	11.73
Acetosacet- β -naphthylamide-S	$C_{14}H_{11}O_3NS$	"	82°	107°	S, 11.26	11.72
Acetosacet-(1:3:4)-xylylide-S	$C_{13}H_{13}O_3NS$	"	90°	102°	S, 12.83	12.75
Acetosacet-(1:4:5)-xylylide-S	$C_{13}H_{13}O_3NS$	Deep brown	97°	114°	S, 13.10	12.75
Acetone dicarboxyanilide-S	$C_{17}H_{14}O_4N_2S$	Fine rosy	140°	170°	S, 9.51	9.36
Acetone dicarboxy-o-toluidide-S	$C_{19}H_{15}O_4N_2S$	Pink	155-56°	174°	S, 8.45	8.64
Acetone dicarboxy-p-toluidide-S	$C_{19}H_{15}O_4N_2S$	Pink	185°	208-10°	S, 8.29	8.64
Acetone dicarboxy- α -naphthylamide-S	$C_{25}H_{18}O_4N_2S$	Greenish brown	137°	155°	S, 7.59	7.24
Acetone dicarboxy- β -naphthylamide-S	$C_{25}H_{18}O_4N_2S$	Crimson	185°	207°	S, 6.99	7.24

The authors take this opportunity to express their gratitude to the Government of His Highness the Maharaja Geakwar of Baroda for a grant which defrayed the expenses incurred in this work.

CHEMISTRY DEPARTMENT,

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Received March 19, 1932.

A Physical Method of Estimating Ferrous and Ferric Iron formed by the Actions of Potassium Dichromate and Potassium Permanganate upon Ferrous Salt.

BY MATA PRASAD AND P. V. DESHPANDE.

• In the present investigation the amounts of ferrous and ferric iron have been determined by the use of absorption spectra. A quartz spectrograph was used. An iron arc consuming three amperes was used as the source of light. A Baly's absorption tube with quartz end-plates was used. The width of the slit, the focus, the necessary aperture and the time of exposure were adjusted by taking some trial spectrograms. Standard solutions of ferrous ammonium sulphate, potassium dichromate and potassium permanganate were prepared from Merck's pure chemicals. After taking the absorption spectra of pure solutions, the ferrous salt solution was mixed respectively with potassium dichromate and potassium permanganate in different known proportions. With single solutions or with mixtures of solutions, the length of the absorption column of the Baly's tube was varied and several photographs were taken. The thickness exposed was then expressed in terms of equivalent thickness of $M/10,000$ solution with respect to iron.

The strength of the mixture has been expressed in terms of its iron contents and it has been called 'molal' when it contains 56 g. of iron in 1000 c.c. of the mixture.

Ferrous ammonium sulphate has only total absorption and when it is mixed with either of the oxidizing salts, they lose their characteristic bands and the mixture gives only total absorption. As the composition of the mixture is changed, the absorption border also shifts. The results of the measurements for various mixtures with potassium dichromate and potassium permanganate respectively are graphically represented in Figs. 3 and 4. In these graphs the logarithm of equivalent thickness for $M/10,000$ mixture has been plotted against the corresponding absorption edge.

The absorption borders of mixtures containing different proportions of potassium dichromate and potassium permanganate were

read at $\log t=4$ from the curves shown in Figs. 3 and 4 and the results are graphically shown in Figs. 1 and 2.

The graphs in Figs. 1 and 2 can be used to determine the percentage of ferrous and ferric iron present in a mixture of known iron content, containing the ferrous salt and either of the oxidizing agents in amounts insufficient to oxidize the whole of the ferrous iron.

The absorption spectrum of a mixture of known iron contents (say 0.048M) containing ferrous ammonium sulphate and potassium dichromate is taken at a thickness $t=1/c$ (where c is the molality of the mixture) and it is assumed that the absorption edge lies at 36660 A.U. From graph in Fig. 1, the proportion of ferrous and ferric iron for this absorption edge is 89.45 to 10.55. Since the total quantity of iron in 1000 c.c. is 2.688 g., the quantities of ferrous and ferric iron are 1.4154 g. and 0.2726 g. respectively.

The results thus obtained have been compared with the theoretical ones. The method can be used for estimation of ferrous and ferric iron in a mixture under the conditions stated.

TABLE I.

Potassium Dichromate.

Theoretically calculated.		Physically determined.	
Fe(ous).	Fe(ic).	Fe(ous).	Fe(ic).
98.24	1.76	98.50	1.50
90.02	9.98	89.40	10.60
80.19	19.81	81.20	18.80
64.80	35.61	65.10	34.90
37.47	62.53	36.99	63.01

TABLE II.

Potassium Permanganate.

Theoretically calculated.		Physically determined.	
Fe(ous)	Fe(ic)	Fe(ous)	Fe(ic)
95.72	4.28	96.10	3.90
75.70	24.30	75.90	24.10
64.37	35.63	64.40	35.60
50.40	49.60	50.60	49.40
30.27	69.73	30.67	69.37

FIG. 1.

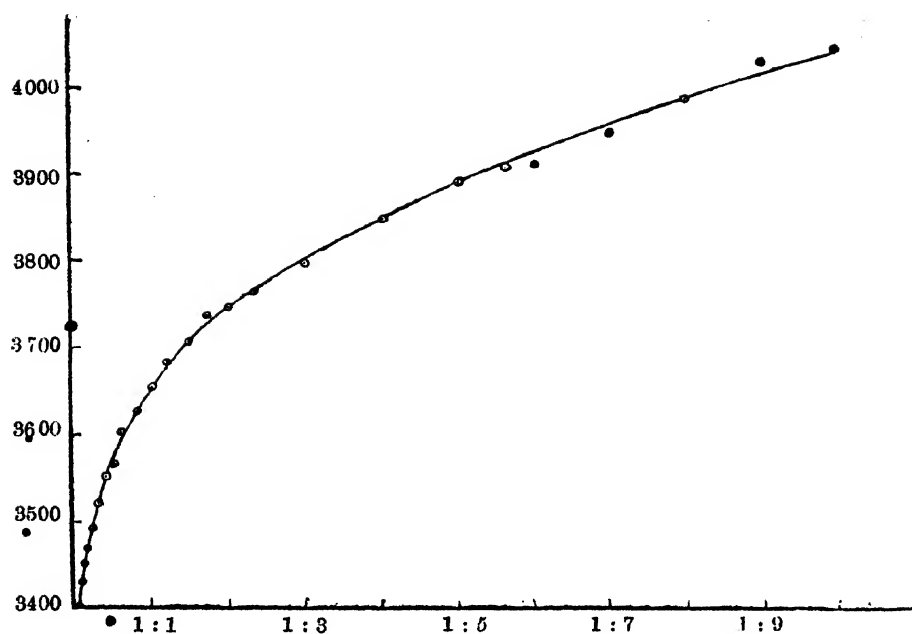


FIG. 2.

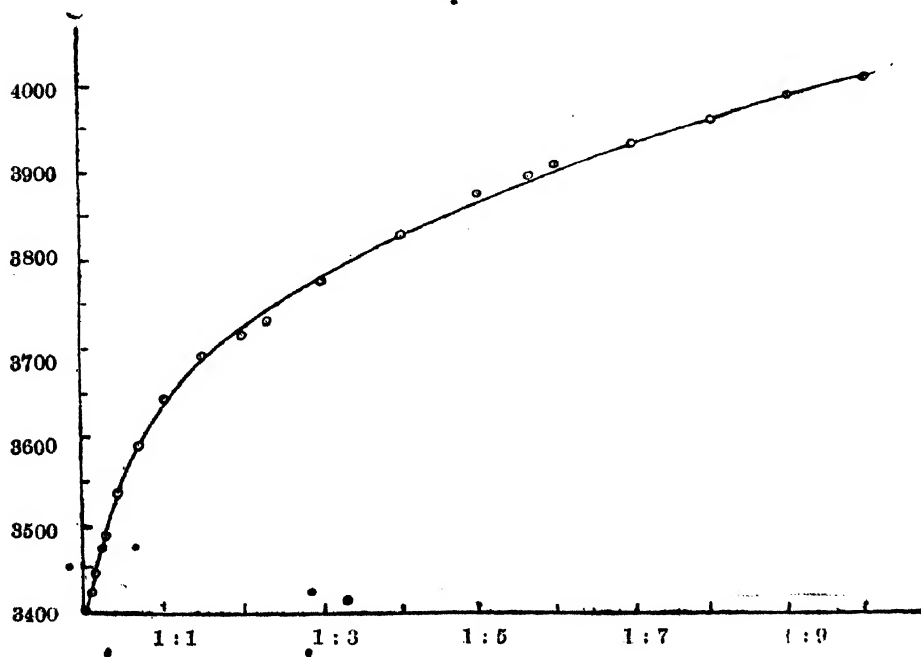


FIG. 3.

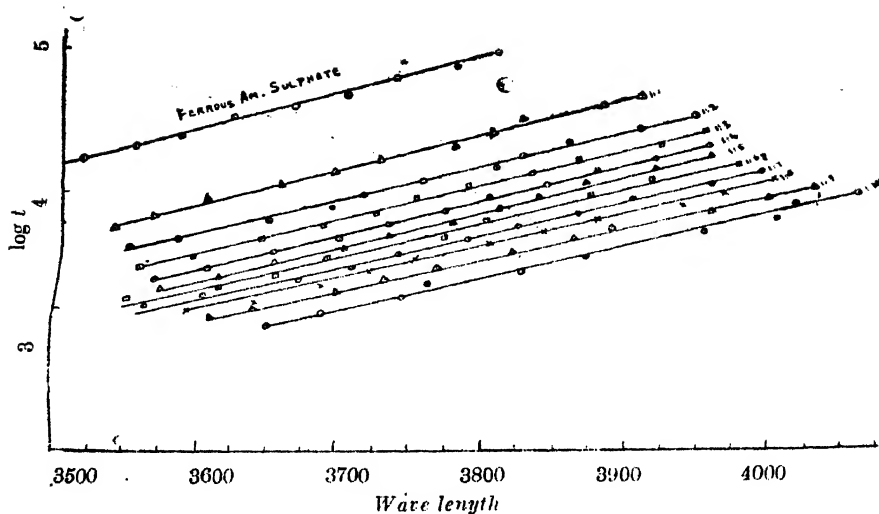
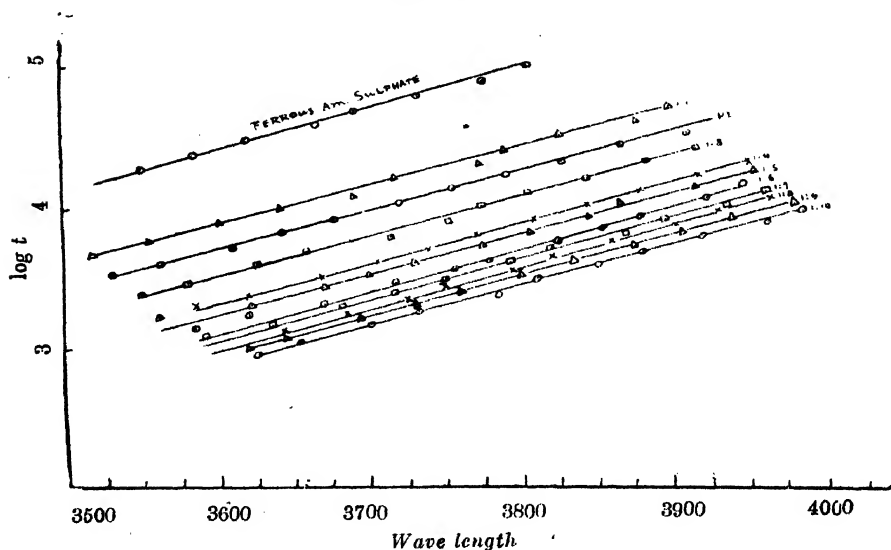


FIG. 4.



The authors wish to express their thanks to Prof. G. R. Paranjpe, Head of the Physics Department for his interest during the progress of the work.

A Note on the Relation between Coagulation and Gelation Points of Sols.

BY SATYA PRAKASH.

Gessner (*Koll. Chem. Beih.*, 1924, 19, 213) found in the case of vanadium pentoxide sol that more electrolyte is necessary to give a jelly of the sol in a definite period than to coagulate it. In this connection, I am submitting some of my observations regarding positively charged sols.

A known amount of the sol was mixed with different concentrations of electrolytes and the volume was kept constant in every case by the addition of water. The sols were allowed to stand for one hour, and the minimum amounts of electrolyte necessary to completely coagulate the sol and to give the jelly in the same period were noted. In the case of lyophilic jelly-forming sols, it is rather difficult to expect that the particles would settle down soon after coagulation, and therefore, the end points for coagulation were taken by filtering the sols and observing that no colloidal phase passes down in the filtrate at the point.

TABLE I.

Time of observation = 1 hour.

Sol.	Days dialysed.	Conc. per litre.	Amount of sol.	Total Vol.	Electrolyte.	Coagulation point.	Gelation point.
			[c.c.]	[c.c.]		[c.c.]	[c.c.]
1. Ferric arsenate	5	30 g.	2.5	5.0	N/5-KCl	0.35	0.45
			3.0	5.0	"	0.40	0.50
			1.5	5.0	N/200-K ₂ SO ₄	0.50	1.10
			2.0	5.0	"	0.60	1.15
			2.5	5.0	"	0.70	1.30
2. Chromic arsenate	6	36.4	4.0	6.0	N/5-K ₂ SO ₄	0.90	1.10
			4.0	6.0	N/10-K ₄ FeCy ₆	0.65	0.80
3. Zirconium molybdate	5	14.48	4.0	6.0	N/20-KCl	0.30	0.40
			4.0	6.0	N/50-K ₂ SO ₄	0.30	1.00
4. Zirconium borate	4	24.72	4.0	6.0	N/4-KCl	0.80	1.20
			4.0	6.0	N/10-K ₂ SO ₄	0.80	1.50
*5. Titanic acid	...	15.02	3.0	4.0	N/50-KCl	0.60	0.70
					N/50-KBr	0.90	1.00
					N/500 K ₂ CrO ₄	0.80	1.00
					N/125-K ₂ SO ₄	0.30	0.50
					N/1000-K ₃ FeCy ₆	0.40	0.50
					N/1000-K ₄ FeCy ₆	0.30	0.40

* cf. Bhatia and Ghosh, *J. Indian Chem. Soc.*, 1930, 7, 687.

Similar results have been obtained with other sols both negatively and positively charged. From these results, it appears that a little more electrolyte is necessary to set a jelly than to coagulate the jelly-forming sol in the same time. The same amount of electrolyte which coagulates a sol in one hour would give the jelly in a period which varies with the purity of the sol. In the case of comparatively impure sols, the period of gelation has been extended from that of a few hours to 24 hours and even more. The effect of purity on the relation of coagulation and gelation points is illustrated in Table II.

A sol of ferric arsenate, containing much excess of ferric chloride was prepared and during the course of dialysis, its gelation and coagulation points and also the concentration of chloride ions were determined.

TABLE II.

Amount of sol taken = 3 c.c. Total volume = 5 c.c. Time = 1 hour.

Days dialysed.	Conc. per litre.	Conc. of chloride ions.	Molar conc. of K_2SO_4		Gelation coagulation ratio.
			to coagulate.	to give jelly	
3	25.68 g	0.077N	0.08M	no jelly	—
10	22.31	0.018N	0.0015M	0.0025M	1.66
11	21.42	0.011N	0.0012M	0.0016M	1.33
12	21.67	0.0085N	0.0008M	0.0010M	1.25
13	23.91	0.0070N	0.0005M	0.00055M	1.10

The results recorded in this table show that as the sol becomes purer, and the concentration of chloride ions becomes less on dialysis, the ratio between gelation and coagulation concentrations approaches unity. In the case of very pure sols, gelation and coagulation points coincide with one another.

The difference between gelation and coagulation points is more marked when the sols are coagulated by bivalent ions than when by monovalent ions, as would be seen from Table III. The results are based on the figures given in the Table I.

TABLE III.

R is the ratio between the gelation and coagulation concentrations.

Sol.	R with KCl.	R with K_2SO_4 .
Ferric arsenate	$0.45/0.35=1.28$	$1.30/0.70=1.85$
Zirconium molybdate	$0.40/0.30=1.33$	$1.00/0.30=3.33$
Zirconium borate	$1.20/0.80=1.5$	$1.50/0.80=1.87$
Titanic acid	$0.70/0.60=1.16$	$0.50/0.30=1.66$

From these results, it would be seen that in all the cases, the value of R is greater when the coagulation is effected by potassium sulphate than when by potassium chloride. •

The author wishes to express his indebtedness to Prof. N. R. Dhar for his very kind interest and guidance in the work.

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A Note on the Liesegang Rings of Silver Chromate in Gelatine.

BY B. N. DESAI AND G. M. NABAR.

• It is well-known that sometimes it is not possible to get Liesegang rings of silver chromate in different samples of gelatine. The explanation of this particular behaviour lies in the observation of Liesegang (*Z. Phys. Chem.*, 1914, **88**, 3) himself who has stated that the best rings are obtained if the gelatine is not too pure and contains suitable amounts of acid and gelatose. The purpose of this note is to give some results which indicate the probable role of the p_H of gelatine on the nature of Liesegang rings of silver chromate.

A 20 per cent. solution of silver nitrate was allowed to diffuse into a 15 per cent. gelatine gel impregnated with 0.1 per cent. of potassium dichromate. The experiments were carried out at a temperature of 28°. The results (mean of three independent experiments) are given in the table at the end of the paper.

The results show that an increase in the acidity of gelatine is accompanied by a decrease (i) in the time after which the first ring appears, (ii) in the distances between the same successive rings and (iii) in the number of rings which can be obtained. The statement that addition of suitable proportions of acid increases the width of the chromate rings until, with excessive amounts, the whole precipitate forms a continuous band (E. Hatschek, "A Laboratory Manual of Elementary Colloid Chemistry" 1920 Ed., p. 125) is not supported by these experiments and it is difficult to understand the reasons of differences in the results in the two cases. A decrease in the distances between successive rings with an increase in the acidity of gelatine might be due to the following effect.

We have shown (paper by Desai and Nabar which is in course of publication in the *Trans. Faraday Soc.*) that the inhibitive power of gelatine increases with a decrease of its p_H (addition of acetic acid) due to an increase in the opposition to the growth of crystallisation centres and that a sample of gelatine with lower p_H can keep a

greater amount of silver chromate in ionic condition than another sample with higher p_H . The degree of supersaturation having increased with an increase in the acidity of gelatine, once a crystallisation centre is formed, both its rate of growth and the ultimate size of the particle of the precipitate will be great. Now an increase in the size of the particles of the precipitate will decrease the adsorption of the substances present in the neighbourhood due to a decrease in the specific surface and hence silver nitrate will not have to travel a great distance before the metastable limit for the appearance of the next ring is reached. It would thus appear that the distances between successive rings will decrease with an increase in the acidity of gelatine due to an increase in its inhibitive power.

With an increase in the acidity of the gel the rings are found to be spiral shaped, broken at places, or are not obtained at all because of the fact that there is a tendency for the particles of the precipitate to become bigger as shown by these results. As pointed out by Bradford (*J. Soc. Chem. Ind.*, 1929, **48**, 79) if the precipitate can be obtained in a fine condition good rings can always be obtained. He achieved this purpose by working with dilute solutions of the reactants or by decreasing the solubility of the precipitate in the gel by adding alcohol to it. One would thus expect that perfectly good rings of silver chromate should be obtained in gelatine having a higher p_H , because the number of crystallisation centres being increased the precipitate will be obtained in a finer condition. But this process cannot probably go on indefinitely. For, as we have shown (Desai and Nabar, *loc. cit.*) increase of p_H causes a decrease in the maximum possible saturation and, therefore, we may expect that ultimately the supersaturation value will coincide with that corresponding to the saturation solubility product. The consequence of this will be that although the precipitate may be in a fine condition it will be deposited more or less in a continuous manner throughout the medium without the formation of rings. The rate of diffusion may also change with a change in the p_H of gelatine and might probably be connected with this. The question, however, requires further investigation. It is possible that there might be definite limits to the p_H value of gelatine within which good rings of silver chromate can be obtained.

We are at present investigating in detail the influence of the inhibitive power of different gels on the formation of banded precipitates of various sparingly soluble substances.

TABLE

p_H of the gel.	Approximate time after which first ring appears.	Distance from the top at which first ring appears.	Distances	between	the	successive	rings.	
			† 1-2	2-3	3-4	4-5	5-6	6-7
5.15	48 hr.	32 mm.	1.2 mm.	2.0 mm.	2.8 mm.	4.2 mm.	6.0 mm.	7.3 mm.
5.10	28	23	*	1.5	2.0	3.0	4.8	...
5.00	13	19	*	*	1.5	2.0	3.0	...
4.00 ^b

Remarks: In the case of the gel having p_H 5.15 the rings were well-defined. In the gel having p_H 5.10 the rings had a tendency to become spiral shaped and after the appearance of the sixth ring no further rings formed but reddish black spherical and thread-like crystals appeared here and there. With gel having p_H 5.00 the rings were not complete but broken at places; after the fifth ring there appeared reddish black spherical and threadlike crystals here and there. Gel having p_H 4.00 did not give any rings but contained reddish black spherical crystals spread here and there. The size of the particles in the rings becomes bigger and bigger as the acidity of the gel increases.

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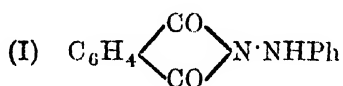
† First ring in each case corresponds to the first band which appears after the initial continuous precipitate as examined under the microscope.

* The rings were not quite well-defined and so it was difficult to measure the distances.

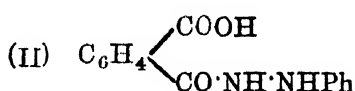
The Reaction between Quinolinic Anhydride and Phenylhydrazine.

BY PREM RANJAN SEN-GUPTA AND ANUKUL CHANDRA SIRCAR.

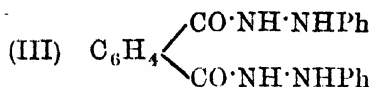
Hötte (*J. pr. Chem.*, 1887, ii, 35, 265, *et seq*) has shown that phthalic anhydride condenses with phenylhydrazine to give four different condensation products under different experimental conditions.



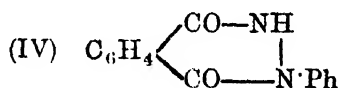
Phthalylphenylhydrazine.



Anilidophthalaminic acid.



Phthalylldiphenylhydrazine
(Dianilinophthalylldiamide).



β -Phthalylphenylhydrazine.

According to Hötte (*loc. cit.*) the compound of type (IV) is formed not by the direct action of one molecule of phenylhydrazine and one molecule of phthalic anhydride but by the elimination of one molecule of phenylhydrazine from a compound of the type (III) first formed.

Ghosh (*J. Chem. Soc.*, 1919, 115, 1103) attempted the condensation of quinolinic acid with phenylhydrazine and obtained a compound of the type (I).

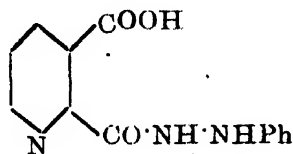
Using different experimental conditions, besides quinolinylphenylhydrazine, compounds of the types (II) and (III) in a very pure condition and most probably a compound of the type (IV) in a somewhat impure condition have now been obtained by the condensation of quinolinic anhydride with phenylhydrazine. In an experiment in which quinolinic acid and higher temperature were used, a new compound, as indicated by its melting point, containing

the same percentage of nitrogen as required by the compound of type (III) was obtained. In view of the fact that at a higher temperature quinolinic acid evolves carbon dioxide and is converted to nicotinic acid it is surmised that the same change took place under conditions of the experiment and the resulting nicotinic acid reacted with phenylhydrazine to form phenylhydrazinonicotinate.

Quinolinic as well as phthalic and naphthalic anhydrides have also been condensed with unsymmetrical methylphenylhydrazine but in each case compounds of the type (I) have only been obtained.

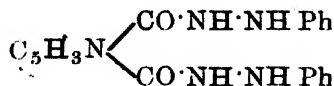
EXPERIMENTAL.

Anilidoquinolinaminic Acid.



Quinolinic anhydride (0.75 g.) was suspended in benzene (10 c.c.) and to this, a solution of phenylhydrazine (0.55 g.) in 5 c.c. of benzene added and the mixture allowed to stand at the ordinary temperature with occasional stirring for 2 days. The separated solid was collected, washed first with benzene, then with a little alcohol and finally crystallised from alcohol in colourless needles, m.p. 146° (decomp.). It is insoluble in benzene, easily soluble in alcohol or acetic acid. It dissolves in sodium carbonate solution. (Found: N, 16.68. $C_{13}H_{11}O_3N_3$ requires N, 16.34 per cent.).

Quinolinylldiphenylhydrazine (Dianilidoquinolinylldiamide).

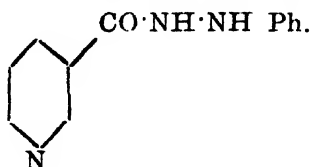


A mixture of quinolinic anhydride (0.7 g.) and phenylhydrazine (0.5 g.) (equimolecular quantities) was heated in a test tube on an oil-bath at 120-30° for 10 minutes and then allowed to cool. The fused mass was dissolved in alcohol. On adding very dilute hydrochloric acid to the solution, a solid separated which crystallised from

alcohol in yellow needles, m.p. 201° . It is soluble in alcohol, acetic acid or pyridine, and insoluble in benzene. It dissolves in strong sulphuric acid with light violet colour which disappears on heating. (Found: N, 20.31. $C_{19}H_{17}O_2N_5$ requires N, 20.17 per cent.).

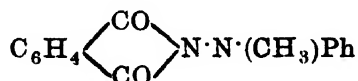
In the anticipation of obtaining β quinolinylphenylhydrazine (i.e., compound of the type, IV), the preceding compound was heated to 200° for 1 hour. It suffered decomposition and phenylhydrazine was given out. But the other resulting product could not be obtained in a sufficiently pure state.

Phenylhydrazinonicotinate.



Quinolinic acid (0.5 g.) with phenylhydrazine (2 c.c.) was heated in a test tube on the oil-bath for 20 minutes at $200-30^{\circ}$. On adding spirit to the resulting product, a yellow compound separated which crystallised from alcohol as yellow plates, m.p. 185° . It is sparingly soluble in cold alcohol, more so in the hot solvent and insoluble in benzene. (Found: N, 20.24. $C_{12}H_{11}ON_3$ requires N, 19.71 per cent.).

Phthalyl- α -methylphenylhydrazine.



The fused mass obtained by heating together methylphenylhydrazine (0.6 g.) and phthalic anhydride (0.7 g.) on an oil-bath at 130° for 10 minutes, was dissolved in alcohol. The crystalline precipitate which separated on the addition of dilute hydrochloric acid to the solution, was finally crystallised from alcohol in yellow rectangular plates, m.p. 124° . It is soluble in alcohol, acetic acid or acetone, and insoluble in benzene or ether. It dissolves in strong sulphuric acid with a pink colour. (Found: N, 11.37. $C_{15}H_{12}O_3N_2$ requires N, 11.11 per cent.).

Quinolinyl- α -methylphenylhydrazine.— Methylphenylhydrazine (0.6 g.) and quinolinic anhydride (0.7 g.) were heated together at 120° for 15 minutes on the oil-bath. The resulting mass was dissolved in alcohol and precipitated from the solution by the addition of dilute hydrochloric acid. It crystallised from alcohol as yellow prisms, m.p. 155°. Its properties are similar to those of the preceding compound. (Found: N, 16.82. $C_{14}H_{11}O_2N_3$ requires N, 16.60 per cent.).

Nphthalyl- α -methylphenylhydrazine was prepared from naphthalic anhydride (1 g.) and methylphenylhydrazine (0.6 g.) in the same way as the two preceding compounds and finally obtained as yellow plates, m.p. 210°. It is soluble in alcohol or acetic acid, more so in the hot solvents and insoluble in benzene. (Found: N, 9.58. $C_{19}H_{14}O_2N_2$ requires N, 9.27 per cent.).

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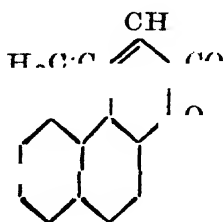
Received March 12, 1932.

Coumarins and Chromones from β -Naphthol.

By BIMAN BIHARI DEY AND ARUPATHI KRISHNASWAMI
LAKSHMINARAYANAN.

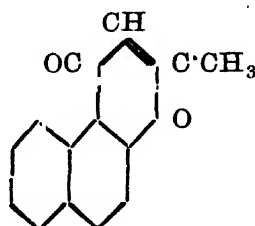
The naphtha- α -pyrone derived from β -naphthol and acetoacetic ester yields smoothly and quantitatively an extraordinarily stable coumarinic (*cis*) acid (Dey, *J. Chem. Soc.*, 1915, 1118, 1620, 1630). As far as we are aware, it provides the only exception to the rule that coumarins as a class, and specially those with an alkyl group in the 4-position, offer considerable resistance to the opening of the pyrone ring by alkalis, and eventually form only *unstable* coumarinic acids which cannot be isolated as such, but are reconverted into the original coumarins on acidifying their alkaline solutions. No plausible explanation of the remarkable stability of the methyl- β -naphthacoumarinic acid has yet been offered and there also remains some uncertainty regarding the constitution of the β -naphthapyrone itself (Dey, *loc. cit.* p. 1615). Further work on the constitution of β -naphthapyrones in general has recently been published (*J. Indian Chem. Soc.*, 1932, 9, 71).

Bacovescu (*Ber.*, 1910, 43, 1280) first prepared a pyrone which was designated 1-methyl-4:3- β -naphthapyrone (*vide, infra*) having the following constitution,



by condensing β -naphthol and acetoacetic ester with the aid of concentrated sulphuric acid, and the same compound was subsequently prepared (Dey, *loc. cit.* p. 1628) by heating 4:3- β -naphthapyrone-1-acetic acid above its melting point (191°). While preparing large quantities of this pyrone, the curious fact repeatedly came to our notice that although the crude material, after washing free from unchanged β -naphthol by alkali, appeared crystalline and fairly pure, and amounted to as much as 75 per cent of the theoretical yield (16 g. of the uncrystallised body were uniformly obtained

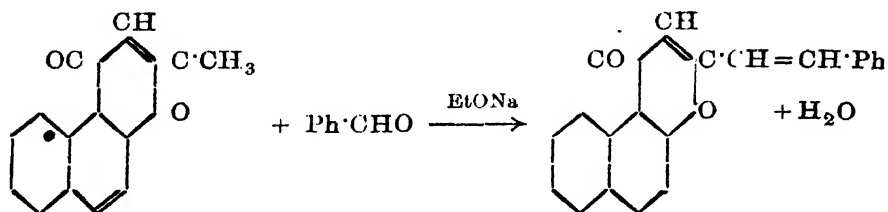
from 14 g. of β -naphthol), the product melted very indefinitely, and the pure β -naphthapyrone (m.p. 179°) ultimately obtained by several recrystallisations of the crude product from boiling alcohol, amounted hardly to 24 per cent (5 g.) of the yield required by theory. The presumption seemed, therefore, to be reasonable that the reaction had led to the formation of some other product or products, the separation of which in a pure state by fractional crystallisation from a suitable solvent or by treatment with alkalis at different temperatures, should be practicable. Attempts at separating the constituents of the mixture by these methods have not yet been successful, but evidence has been obtained from other directions which has settled definitely the nature of the second component. The possibility that the impurity in the present case might consist, at least to some extent, of the corresponding β -naphthachromone derivative suggested itself quite early in the investigation, and a reference to literature showed that the expected methyl- β -naphthachromone, which is designated 3-methyl-1:4- β -naphthapyrone* having the following constitution



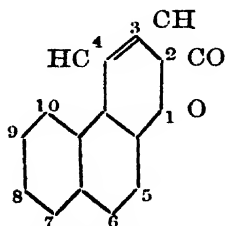
had already been described by several investigators. It appears to have been first synthesised by Schneider and Kunau (*Ber.*, 1921, **54**, 2302) by condensing β -naphthylmethylether with sulphoacetic acid (a mixture of acetic anhydride and sulphuric acid) and treating the resulting 2-acetyl-3-methyl-1:4- β -naphthapyrone (m.p. 157°) with alcoholic ammonia, when the desired naphthachromone (m.p. 168°) was obtained. Wittig (*Annalen*, 1925, **446**, 155) subsequently prepared the same compound by heating 1-aceto-2-naphthol with sodium acetate and acetic anhydride, a mixture of the 2-acetyl derivative (m.p. 157°) and the methyl- β -naphthachromone (m.p. recorded

* There seems to exist some confusion in the method of nomenclature of these bodies. The names β -naphthacoumarin and β -naphthachromone chosen by Bartsch (*Ber.*, 1903, **36**, 1969), Bacovescu (*loc. cit.*), Schneider and Kunau (*loc. cit.*), and others are obviously unsuitable, while the designations 1-methyl-4:3- β -naphthapyrone (Dey, *J. Chem. Soc.*, 1915, **115**, 1629) for the coumarin, and 3-methyl-1:4- β -naphthapyrone (Menon and Venkatarāman, *J. Chem. Soc.*, 1931, p. 2894) for the

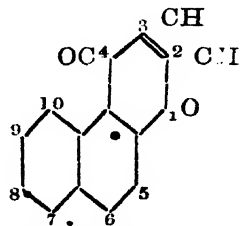
by Wittig is 164°) being obtained. Recently Menon and Venkataraman (*J. Chem. Soc.*, 1931, p. 2594) prepared the above mentioned 2-acetyl derivative by the same method as that described by Wittig, and obtained from it the pure β -naphthachromone (m.p. 168°) by deacetylating it with alcoholic ammonia according to the directions given by Schneider and Kunau (*loc. cit.*). The constitution of this methyl- β -naphthachromone would thus appear to have been well established by these syntheses, and the same compound has now been synthesised from β -naphthol and acetoacetic ester by using phosphorus pentoxide as the condensing agent (Simonis' method). The chromone is best characterised by conversion into the 2-styrene derivative which is formed with extreme readiness and separates in almost quantitative yield from alcohol according to the following equation (*cf.* Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, 123, 2565).



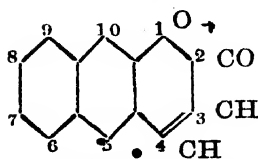
corresponding chromone, do not convey a clear idea of the relationship between the structures of these two bodies. The following system of naming the coumarins and chromones derived from β -naphthol seems to have the advantage of being more consistent and has been adopted by us in the present paper:—



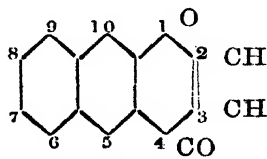
1:2- β -Naphthapyrone.



1:4- β -Naphthapyrone.



1:2- $\beta\beta$ -Naphthapyrone.



1:4- $\beta\beta$ -Naphthapyrone.

The reaction with benzaldehyde thus affords a suitable test for detection of the chromone even when it occurred in minute quantities, and was therefore applied to the determination of its presence in the crude mixture obtained by the condensation of β -naphthol and acetoacetic ester by means of sulphuric acid. On treating a warm alcoholic solution of the crude material with benzaldehyde followed by the addition of a slight excess of alcoholic sodium ethoxide, considerable quantities of the sparingly soluble styrene (m.p. 198°), identical in all respects with that derived from the chromone, crystallised out in the course of an hour. The pure β -naphtha-1:2-pyrone (m.p. 179°), however, when treated in the same way, gave no sign of reaction or formation of a benzylidene derivative, and on expelling the unchanged benzaldehyde with steam, and acidifying the cold alkaline solution, the stable coumarinic acid, mixed with a little unchanged coumarin, slowly separated out.

These results seem to be of particular interest in their bearing on the problem of syntheses of coumarins and chromones by Pechmann's and Simonis' methods respectively. They prove conclusively that coumarins and chromones may *both* be formed under the conditions of Pechmann's reaction in which strong sulphuric acid is used as the condensing agent. This fact does not appear to have been noticed or given due prominence by any of the workers who have recently invaded this field, and it may therefore be not out of place here to dwell briefly on the history of this reaction. Simonis (Petscheck and Simonis, *Ber.*, 1913, **46**, 2015; Simonis and Lehmann, *Ber.*, 1914, **47**, 697; Simonis and Remmert, *ibid.*, 1914, **47**, 2229) first claimed to have made the observation that chromones and not coumarins were formed when, in the usual Pechmann reaction, concentrated sulphuric acid was replaced by phosphorus pentoxide in dry ether. In a series of papers published by Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 425, 959, 1051; Ghosh, *ibid.*, 1915, **109**, 105) the claim was made that chromones had been synthesised even by the use of sulphuric acid. According to these authors the formation of coumarins or chromones in the ordinary Pechmann synthesis seemed to depend on the nature of the β -ketonic ester or the β -diketone molecule, chromone formation being favoured by the substitution of one of the methylene-H atoms by an alkyl or other complex groups. These statements remained unchallenged until Baker and Robinson (*J. Chem. Soc.*, 1925, **127** 1981; Baker, *ibid.*, 1925, **127**, 2849) threw doubt on the authenticity of the so-called chromones synthesised by Jacobson and Ghosh, and

succeeded in proving definitely that the supposed chromones were in reality coumarins. Since then Chakravarti (*J. Indian Chem. Soc.*, 1931, 8, 129, 407) and Robertson and others (*J. Chem. Soc.*, 1931, p. 1256, 1877, 2426) have published much valuable data concerning the Simonis reaction and shown that the generalisation made by Simonis is by no means justified, chromones being formed in only a very limited number of cases, *e.g.*, those of phenol itself, catechol, guaiacol, *p*-cresol and quinol, while with other phenols and with α -naphthol, the products were only coumarins. Robertson and others seem to have arrived at the conclusion that while coumarins are exclusively formed by Pechmann's method, the use of phosphorus pentoxides as the condensing agent results, in a few rare instances, in the formation of chromones, the course of the latter condensation being determined by the nature of the phenol rather than by that of the β -ketonic ester employed.

In the light of the observations made with β -naphthol which are now recorded, the conclusion is unavoidable that the proposition of Ghosh and Jacobson, *viz.*, that coumarins and chromones may both be formed in the normal Pechmann process, is fundamentally sound. The important factor which determines the course of the condensation, however, is obviously not the β -ketonic ester but the phenol itself, as suggested by Robertson. It seems to be peculiarly unfortunate that the large number of incorrect observations recorded by Jacobson and Ghosh, the majority of the compounds described by these authors as chromones having now been proved to be the corresponding coumarins, should have misled chemists into doubting the possibility of their fundamental assumption, *viz.*, that chromones are formed even through the agency, of sulphuric acid, being correct.

EXPERIMENTAL.

Preparation of 4-methyl- β -naphthacoumarin (4-methyl-1:2- β -naphthapyrone) by a slight modification of the experimental conditions given by Bacovescu (loc. cit.).—A mixture of finely powdered β -naphthol (14 g.) and ethyl acetoacetate (15 g.) was slowly added to ice-cold concentrated sulphuric acid (25 c.c.) and shaken vigorously. After 24 hours, excess of cracked ice was added, and the precipitated gummy mass washed repeatedly with cold water and finally with 20 p.c. methanol when it became granular and easy

to filter. It was then left in contact with $N/2$ -caustic soda for some hours, filtered, washed with water and dried. The pale yellow crystalline solid weighed 16 g. approximately, and melted indefinitely between 125° and 160° . The pure coumarin was obtained by washing the crude material with cold methanol and then crystallising twice from excess of boiling absolute alcohol with the aid of animal charcoal. Colourless plates, m. p. 179° , yield 5 g.

Synthesis of 2-methyl-1:4- β -naphthapyrone from β -naphthol and ethyl acetoacetate.—Powdered β -naphthol (8 g.) and ethyl acetoacetate (7.5 g.) were warmed in a flask until a clear solution was obtained, and dry phosphorus pentoxide (15 g.) quickly added and thoroughly mixed. The reaction began almost immediately, but it never became violent and no cooling was found necessary. The mixture was finally heated on the water-bath for 20 minutes, and on cooling, ice-water (200 c.c.) was added, the whole thoroughly stirred and allowed to stand for 2 hours. A dark tar was deposited which, on rubbing repeatedly with N -caustic soda, gradually solidified. It was washed with a little cold methanol, and then crystallised twice from the boiling solvent with animal charcoal. Colourless rectangular plates, m. p. 169° , yield 1.2 g. (Found: C, 80.1; H, 5.0. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.76 per cent.). Admixture with the corresponding coumarin (m. p. 179°) depressed its melting point to 140° . The substance dissolves in concentrated sulphuric acid to a pale yellow solution which exhibits a bright blue fluorescence (cf. Menon and Venkataraman *loc. cit.*).

2-Styryl-1:4- β -naphthapyrone.—Naphtha- γ -pyrone (2 g.) was dissolved in boiling absolute alcohol (40 c.c. approx.) and the clear hot solution treated successively with benzaldehyde (2 g.) and a solution of sodium ethoxide prepared from 0.5 g. of sodium and 20 c.c. absolute alcohol. The colourless solution immediately turned yellow which gradually changed to an intense red colour. The liquid was refluxed on the water-bath for 15 minutes and allowed to cool when the flask became filled in a short time with a mass of soft yellow needles. One crystallisation from boiling alcohol gives the pure styrene, m.p. 198° , yield, nearly 2 g. (Found: C, 83.9; H, 4.6. $C_{21}H_{14}O_2$ requires C, 84.6; H, 4.7 per cent.).

The styrene dissolves in concentrated sulphuric acid with a red colour and the solution shows a green fluorescence. Alkaline permanganate is decolourised on shaking with an alcoholic solution of the styrene, manganese oxides being precipitated.

The *dibromide*, prepared by dissolving the styrene (0.5 g.) in warm carbon disulphide (40 c.c.), adding a solution of bromine (0.5 g.) in CS_2 (5 c.c.), and shaking for 1 hour, crystallises from hot glacial acetic acid in yellow plates, m.p. 175° (not analysed).

Interaction of 4-methyl-1:2- β -naphthapyrone and benzaldehyde.—An alcoholic solution of the coumarin was treated with benzaldehyde and sodium ethoxide in exactly the same way as that described in the case of the chromone. The solution became bright yellow but did not turn red. Nothing separated even on standing for 2 days. The alcohol was partly driven off, the benzaldehyde removed with steam, and the cold solution acidified. The solid which was precipitated slowly, was found to dissolve only partly in cold sodium bicarbonate. The insoluble portion, on crystallisation from alcohol, melts sharply at 178° , not depressed by admixture with the pure coumarin. The bicarbonate solution, on acidification in the cold, slowly deposited a solid in the crystalline condition. It melts at $143\text{--}44^\circ$ with sudden effervescence and the residue which quickly solidified, melts at 178° . It thus proves to be identical with the β -naphthacoumarinic acid (β -2-hydroxy-1-naphthylcrotonic acid), m.p. 146° (described by Dey, *loc. cit.*, 1630).

Condensation of the impure (uncrystallised) coumarin obtained from β -naphthol and ethyl acetoacetate with benzaldehyde.—The same conditions as those employed in the previous cases were observed. The mixture changed colour in precisely the same manner as that noticed with the chromone, and on standing for an hour, the characteristic needles of the styrene separated out almost completely. 4G. of the crude coumarin gave nearly 0.8 g. of the pure styrene derivative, m.p. 198° .

The investigation is in progress.

Studies in the Coagulation of Colloids from the Stand-point of Smoluchowski's Theory. Part III.

Coagulation of Arsenious Sulphide Sol by Sulphuric Acid Solutions.

BY SHRIDHAR SARVOTTAM JOSHI AND GURUDAS RAMCHANDRA PHANSALKAR.

It was found in Part II (*J. Indian Chem. Soc.*, 1931, 8, 337) that in the slow coagulations of the arsenious sulphide sol, using dilute sulphuric acid solutions, the diminution of β , the Smoluchowski's constant occurred mainly during the early stages of coagulation. As this conclusion is contrary to the results of some workers (*loc. cit.*) it has been examined here in more detail.

EXPERIMENTAL.

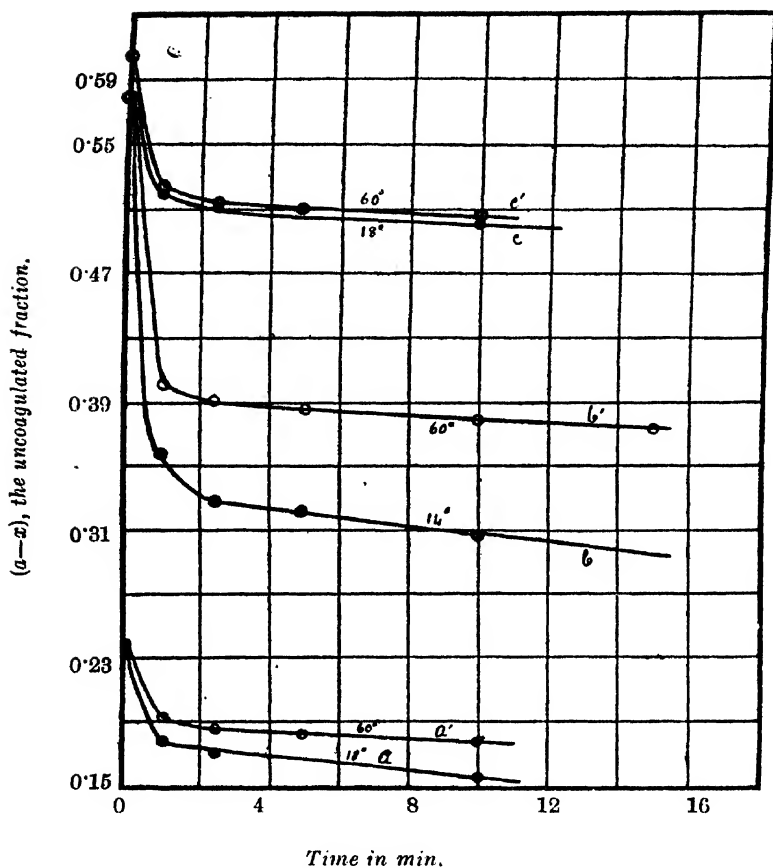
The experimental procedure, the method of preparing the sol, of measuring (a) and ($a-x$), the colloid content at the beginning, and at a time t after the start of coagulation respectively, were the same as in Part II. The results in Tables I—III and in Fig. 1 refer to coagulations at 18° and 60° for different colloids and electrolyte concentrations. β , and k the bimolecular constant, were calculated from $\beta = 1/t \left[\sqrt{\frac{n_0}{n_t}} - 1 \right]$ and $k = \frac{1}{t} \cdot \frac{x}{(a-x)}$ respectively.

The results under β_{T_1}/β_{T_2} in tables relate the observed influence of temperature on β , with that deduced from Smoluchowski's theory (*vide infra*). Curves in Fig. 2 indicate the variation of β during coagulation in different experiments deduced from data in the tables and Fig. 1.

Discussion.

The results show that the rate of coagulation is increased by increasing the temperature. This is contrary to the observations of Linder and Picton (*J. Chem. Soc.*, 1905, 87, 1906) on the coagulation of the arsenious sulphide sol by dilute sulphuric acid at 13° and

FIG. 1.



Curves c, c' cf. Table I.

b, b' II.

a, a' III.

70°. They found that the coagulating concentration was greater at the higher temperature. No definite details as regards the colloid and coagulator concentration as used by them are available. It would appear, however, that the result is not above criticism, since the degree of coagulation was measured by an indirect turbidity method.

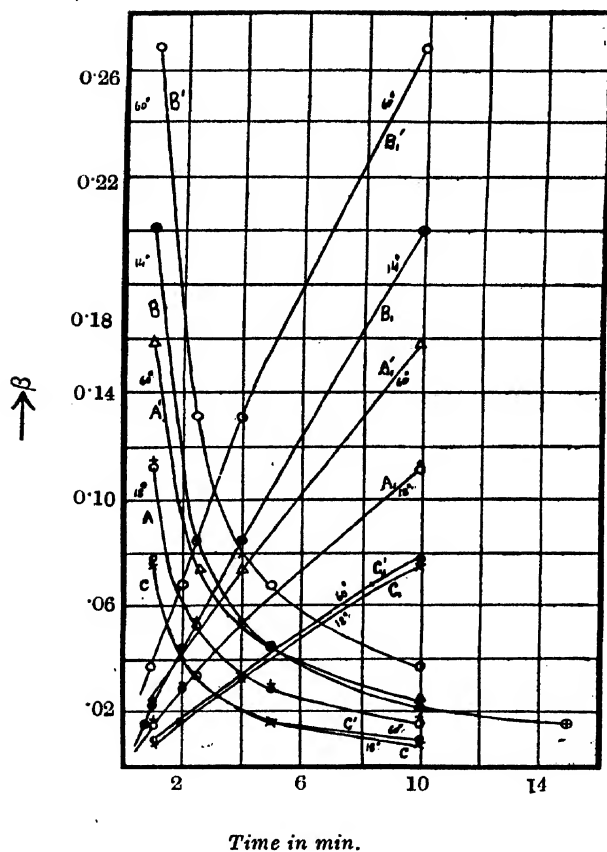
In agreement with previous results the coagulation—time curves in Fig. 1 show that the process cannot be regarded as autocatalytic, although no special precautions were taken to prevent the formation of any coagulation nuclei in the system by stirring etc.

These results also show that the influence of temperature in increasing the rate of coagulation depends on the colloid concentration (*cf.* curves, *a, a'* and *c, c'*, Fig. 1) when that of the coagulator is constant. That the last quantity is also a determinant of the temperature influence on coagulation is apparent from curves, *b, b'*, Fig. 1. This departs markedly from those, characteristic of molecular chemical reactions, and also from the simple mechanism of the coagulation process contemplated in Smoluchowski's theory (*Z. Phys. Chem.*, 1917, **92**, 129). According to this theory β at two temperatures T_1 , and T_2 , is given by $\frac{4}{3} \frac{RT_1}{N_0} \cdot \frac{\eta_0}{\eta_1}$ and $\frac{4}{3} \frac{RT_2}{N_0} \cdot \frac{\eta_0}{\eta_2}$ where η_1 and η_2 are the viscosities of the medium corresponding to T_1 and T_2 , respectively. It must be pointed out here, that in deriving the above equation it has been tacitly assumed that temperature has no influence on a factor ϵ which denotes the probability of coalescence between two colloid particles in the coagulating sol.

It is well known that different coagulators do not alter the coagulation rate to approximately the same extent, or even always in the same direction, as the temperature is increased. The above equation, however, implies that the temperature coefficient of β depends only on the viscosity and the temperature of the medium, and is therefore independent of the nature both of the coagulator and of the colloid. The observed departure from Smoluchowski's theory, as regarding the temperature influence can be explained therefore by considering ϵ , as determined mainly by the ionic adsorption, and therefore a function of the nature of the colloid and of the coagulator; ϵ is therefore variable with temperature (*cf.* Part I. *J. Indian Chem. Soc.*, 1931, **8**, 11). The results under k and β show that contrary to the requirements of Smoluchowski's theory, and in agreement with general results on slow coagulation, these quantities diminish during coagulation.

The diminution of β during coagulation would appear to be mainly due to diminution of ϵ . As there is not much information in the literature on this point, it is interesting to see that the time variation of β in all the coagulations studied is characterised by regular curves, *A, A', B, B', C, C'*, in Fig. 2. It is seen from these data and in agreement with previous results (Part II. *loc. cit.*) that the diminution of β is appreciably greater during the earlier stages of coagulation than later. •

FIG. 2.



Curves C, C', C₁ & C'₁ relate β with t and $1/t$ [curves c, c' Fig. 1].

B, B', B₁ & B'₁

[b, b'].

A, A', A₁ & A'₁

[a, a'].

TABLE I.

0.125 N/H ₂ SO ₄ . 1 c.c. of K ₂ Cr ₂ O ₇ = 0.001683 g. As ₂ S ₃ .		Initial colloid conc. = 1.21 g. As ₂ S ₃ per litre.		β_{T_1}/β_{T_2}		Initial colloid conc. = 1.21 g. As ₂ S ₃ per litre.	
Time in min.	Titre in c.c. dichromate solution.	18°	60°	18°	60°	obs.	cal.
0	7.19
1	6.22	6.17	5.19	.075	.079	1.05	...
2.5	6.10	6.10	5.13	.084	.084	1.00	.166
5	...	6.05	5.09018072
10	6.01	5.96	5.06	.009	.010	1.11	.038
							.020

TABLE II.

0.204 N/H ₂ SO ₄ . 1 c.c. of K ₂ Cr ₂ O ₇ = 0.001525 g. As ₂ S ₃ .		Initial colloid conc. = 1.16 g. As ₂ S ₃ per litre.	
Time in min.	Titre in c.c. dichromate solution.	14°	60°
0	7.60	.580	...
1	5.27	.402	.268
2.5	5.15	.393	.181
5	5.05	.385	.068
10	4.98	.380	.037
15	4.89	.373	...

TABLE III.

0.125 N/H ₂ SO ₄ . 1 c.c. of K ₂ Cr ₂ O ₇ = 0.001683 g. As ₂ S ₃		Initial colloid conc. = 0.48 g. As ₂ S ₃ per litre.	
Time in min.	Titre in c.c. dichromate solution.	18°	60°
0	2.85	.240	...
1	2.31	.178	.161
2.5	2.21	.186	.074
5	2.17	.183	.039
19	2.13	.178	.016

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Explosion of Oxy-hydrogen Mixtures in Soap Bubbles.

By ANATH NATH MITRA, HARENDRA NATH CHATTERJEE, AND
HEMENDRA KUMAR SEN.

The ignition temperature of inflammable gas mixtures has been determined in various ways, *e.g.*, (i) by enclosing or passing the gas mixture into a heated vessel ; (ii) by direct contact with a hot surface at any point of the inflammable mixture ; (iii) igniting by adiabatic compression ; (iv) by an electric spark.

In (ii) and (iv) almost instantaneous ignition is secured, while in the other methods a time-lag is present. To secure instantaneous ignition, soap bubbles full of inflammable gas mixtures were ignited by McDavid (*J. Chem. Soc.*, 1917, 111, 1003) by touching these bubbles with a hot surface. The divergence in the results obtained by different authors is to be referred to the different methods adopted to cause ignition. The irreproducibility of McDavid's figures using different sources of ignition indicates the futility of attempts to establish ignition temperatures, as a physical constant, unless under similarly maintained conditions. The maintenance of exactly similar conditions in the ignition of gaseous mixtures, is hardly feasible in practical problems of mine explosions, and other similar accidents. The stationary method of ignition is of considerable practical importance, but the determination of the lowest ignition temperature under such circumstances is of still greater consequence.

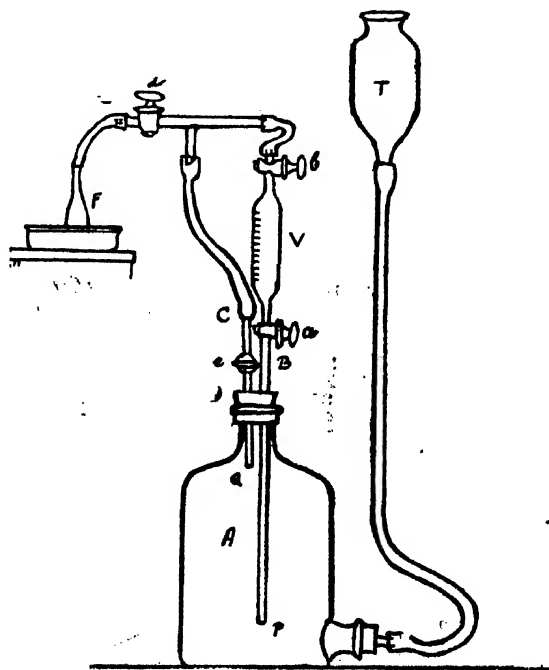
In the present paper we have determined the effect of the volume of soap bubbles on their ignition temperatures. The ignition was effected by touching the soap bubbles either by an electrically heated platinum point formed by bending a wire at an acute angle, or by a platinum spiral (Chatterjee and Sen, *J. Indian Chem. Soc.*, 1929, 6, 441). We have, further, investigated the effect of the length of the platinum wire on the ignition temperature. By varying the platinum wires or using the same wire after roughening it by gently filing, or platinising it, or poisoning it by sulphuretted hydrogen we have come to the conclusion that this method of finding the ignition temperature of an inflammable gas mixture in soap bubbles is unreliable on account of the catalytic effect of the wires.

The temperature of the point or the spiral of platinum wire was determined by reference to a curve plotted with the currents necessary to melt known substances against their respective melting points when they are placed on the platinum point or spiral. The platinum point or spiral is enclosed on all sides except the front by a card board box. The working room has an asbestos ceiling and the doors and windows are kept closed thereby minimising air-currents during the experiment. Each day, however, fresh calibrations were made, although it was found possible to work several days with the same calibration if the wire was not changed, or the atmospheric condition did not change considerably.

In order to ensure reproducibility of results, the volume of the soap bubble had to be kept the same. For this, a special apparatus was devised (*vide, supra*) which enabled us to secure identical volumes and to vary the volumes of the soap bubbles as desired.

The heating current was measured accurately with a standard resistance and a standard cell by the potentiometric method. A set of secondary batteries was used for heating the platinum wire. The volume of the bubbles was controlled by the apparatus (Fig. 1) described below:

Fig. 1.



A is a 5-litre aspirator and *V* a graduated tube holding 1 litre. The whole apparatus is first filled with water and gas is then admitted through *d* until most of the water is displaced, the thistle-funnel *F* being temporarily removed. In order to blow a bubble, *c* is closed, *b* and *d* are opened with the mouth of *F* just on the surface of the soap solution and water is run from *T* to a given mark on *V*, *a* serving to regulate the flow, and the excess gas being allowed to escape. *F* is then removed from the solution with a film over its end and a bubble of required size blown by admitting the corresponding quantity of water into *V*. When all the gas in *V* has been used, a further supply is admitted from the aspirator by opening *c*.

A bottle was filled to about three fourths of its capacity with distilled water. One volume of glycerine was added to 3 volumes of a 2½ p.c. sodium oleate solution, shaken vigorously and kept in the dark for a week. In making large bubbles, sodium oleate weighing about one twentieth of the water taken was found more suitable.

With variations in the oxygen hydrogen ratio, the formation of hydrogen peroxide and ozone was indicated. An approximate yield of hydrogen peroxide and ozone (neglecting the catalytic effect of the vessel itself in destroying them) was obtained as follows:—A steel cylinder of an internal diameter 1½" and a foot long was capped at both ends by reducing sockets, one having an insulated platinum wire introduced for the purpose of supplying the heating source. Both ends had stopcocks and lead-outs and the apparatus was tested for gas tightness before the inflammable mixture was exploded in it. The explosion vessel was first filled with water and then the gas mixture was introduced by displacement of water. After explosion, the stopcock at one end was opened, keeping the end dipped into a solution of potassium iodide. The solution was well-shaken in the explosion tube, run out into a beaker, the explosion vessel was repeatedly washed with water, and the whole solution titrated by means of a *N*-100 sodium thiosulphate solution. 315 C.c. of a gas mixture having equal volumes of hydrogen and oxygen in it, corresponded to 0.3 to 0.4 c.c. of *N*/100 thiosulphate solution. The mixture containing one volume of hydrogen and half a volume of oxygen similarly exploded, curiously liberated no iodine, although traces of both hydrogen peroxide and ozone were obtained in the explosion of the same mixture in soap bubbles.

The formation of hydrogen peroxide and ozone in soap bubble explosions was detected by introducing test papers into the

stem of the thistle funnel, or by interposing the corresponding test solution in the system. The reagents used for the purpose were an alcoholic solution of tetramethyldi-*p*-diaminodiphenyl methane (a name abbreviated to tetramethyl base), and a solution containing a mixture of ferric chloride and potassium ferricyanide (Arnold and Mentzel, *Ber.*, 1902, **35**, 1324 ; Kaiser and McMaster *Amer. Chem. J.*, 1908, **39**, 96). Oxy-hydrogen mixtures in the ratio of 8:2 or 7:3 gave no test for hydrogen peroxide or ozone. In 3:2, 2:1, and 1:1 mixtures both ozone and hydrogen peroxide are present in increasing quantities when such mixtures are exploded. This shows the formation of ozone when hydrogen is burnt which is ascribed to wrong observation by some.

Although under strictly identical conditions, reproducible ignition temperatures are obtainable by this method, the temperature depends on the length and shape of the wire and varies considerably, amounting from 200° to 300° at times. With platinum, the surface seems to affect the temperature ; thus a 5" wire which had been in use for over a year, could ignite large soap bubbles at a constant temperature of 618°, whilst a new 6" wire ignited bubbles of identical size at the constant temperature of 355°. The catalytic nature of the surface is rendered further evident when the surface of the wire is roughened by rubbing with emery paper, or dipped in platinic chloride solution and ignited afterwards by passing a strong current. In both cases, there is a distinct drop in the ignition temperature.

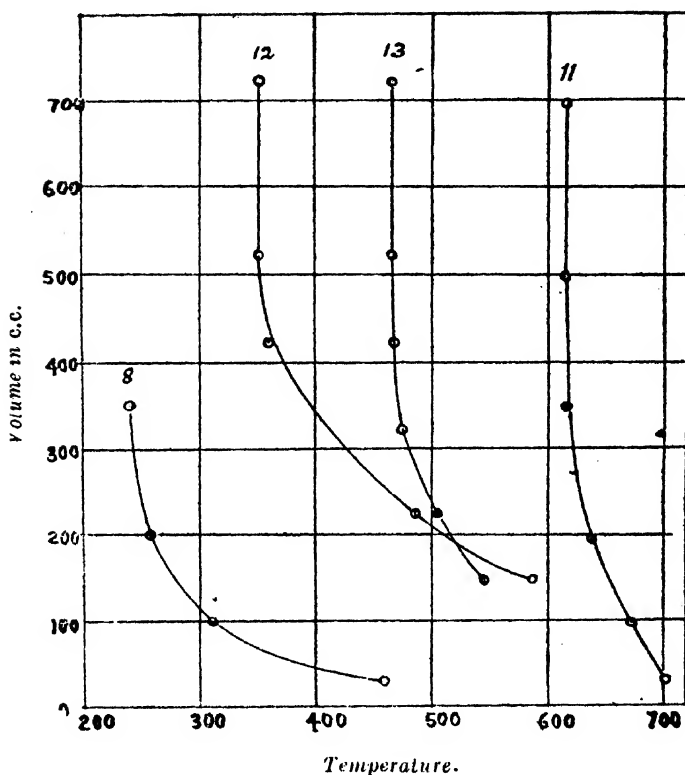
Gas mixture ($H_2:O_2$)=1:1.

Vol. of the bubble = 40 c.c.

<i>Exp. I.</i>				<i>Exp. II.</i>		
	Angle.	Length.	Temp.	Angle.	Length.	Temp.
New wire	30°	2"	570	60°	1½"	564°
Roughened wire	"	"	538°	"	"	545°
Platinised wire	"	"	500°	"	"	527°

It was found that the ignition temperature of small bubbles was greater than that of larger bubbles but as the volume increases further, the ignition temperature approaches a constant value as may be seen from Fig. 2. This is important both from the theoretical as also from the practical points of view. It would appear that approximately 500 c.c. is the critical volume at or beyond which

FIG. 2.



there is no change in the ignition temperature for the same ignition source under any particular set of conditions. A perceptible lag is noticed in the experiments with larger bubbles. This may be compared to the stationary stage of a chain reaction, whilst the explosion to the non-stationary stage (Hinshelwood, *Proc. Roy. Soc.*, 1929, A, 122, 610). In ordinary language, one could say that the catalytic reaction initiated in the preflame period, being exothermic, affords sufficient heat to accelerate the chemical reaction to the stage of explosion, the large size of the bubble imparting to it a more insulated condition and hence a lowered ignition temperature. An alternative explanation, both as regards the constancy of ignition temperature as also its lowering, may be found in the reduced thickness of the soap film with increase in the size of the bubbles. As this would mean virtually the non-existence of any dividing septum between the gas volume and the source of ignition, a uniform ignition temperature is to be expected. This does not explain the remarkably

low temperature of ignition, for which we have to depend upon the preflame period or the generally insulated nature of the soap bubbles when they are large. In fact, to these conditions must be added also the catalytic behaviour of the wires themselves.

EXPERIMENTAL.

(1) Coil on silica strip. Length of pt. wire, 6". Vol. of the gas mixture, 35 c.c.

Comp. of gas mixture (H : O)	7 : 3	2 : 1	3 : 2	1 : 1	2 : 3.
Temp.	712°	708°	720°	750°	782°.

(2) Coil on mica strip. Length of pt. wire, 6". Vol. of the gas mixture, 35 c.c.

Comp. of gas mixture (H : O)	9 : 1	8 : 2	7 : 3	2 : 1	3 : 2	1 : 1	2 : 3.
Temp.	747°	743°	750°	754°	757°	758°	765°

(3) Point source. Angle of the point 30° (approx.). Vol. of the gas mixture, 35 c.c. Length of the pt. wire, 6".

Comp. of gas mixture (H : O)	7 : 3	2 : 1	3 : 2	1 : 1	2 : 3.
Temp.	627°	616°	568°	605°	616°.

(4) Point source. Angle at the point 90° (approx.). Vol. of the gas bubble, 35 c.c. Length of the pt. wire, 6".

Comp. of gas mixture (H : O)	7 : 3	2 : 1	3 : 2	1 : 1	2 : 3
Temp.	665°	642°	628°	607°	609°

(5) Point source. Angle 120° (approx.) Length of the platinum wire, 6". Volume of the gas bubble, 35 c.c.

Comp. of gas mixture (H : O)	3 : 2	1 : 1	2 : 3	3 : 7
Temp.	650°	647°	639°	726°

(6) Point source. Angle at the point, 90°. Length of the platinum wire (new) 2½". In this experiment, the results of which are shown in Fig. 2 (curve 8) the change of the ignition temperature with the change of volume of the soap bubble was investigated, the composition of the gas mixture being as 1 : 1 of hydrogen and oxygen.

(7) Point source. Angle 90° . Length of the platinum wire (new), $4\frac{1}{2}$ ". Volume of the gas bubble, 35.0 c.c. Composition of the mixture, 1: 1. Ignition temperature 538° . The influence of the length of the wire is very clear from the above data, as with a $2\frac{1}{2}$ " wire (Expt. 8) for the same composition and volume, the ignition temperature was only 465° .

(8) Coil on silica strip. Length of platinum wire 9". With a 1: 1 mixture of hydrogen and oxygen, ignition temperatures, 775° , 701° , 668° , 656° were obtained for volumes 35, 150, 250 and 350 c.c. respectively.

(9) Coil on silica strip. Length of the wire, 5". Composition of the gas mixture 1: 1. The results of this experiment are shown in Fig 2 (curve 11).

(10) Coil on silica strip. Length of the platinum wire, 6", but the wire was new. The composition of the gas mixture, the same as before, i.e., 1: 1. Fig. 2 (curve 12).

(11) Point source. Angle 30° approx. Length of the platinum wire (new), 6". Composition of the gas mixture 1: 1. Fig. 2 (curve 13).

From Fig. 2, the attaining of a constant ignition temperature after the bubble has reached a volume of about 500 c.c. is seen.

Reproducibility of results is evident from the following experiments.

1. (a) Point source, angle 30° , 6" pt. wire, 0.2mm. diam.

(b) 150 c.c. bubble exploded at 551° .

(c) After two months with same wire and 30° angle, 150 c.c. bubble exploded at 550° .

2. (a) $2\frac{1}{2}$ " wire, diam. 0.2mm., point source, angle 90° . 100 c.c. bubble exploded at 318° .

(b) $2\frac{1}{2}$ " wire taken from the same reel as (a) with point source, angle 90° exploded at 320° .

Summary.

The results recorded in this paper and the previous one (Sen and Chatterjee, *J. Indian Chem. Soc.*, 1929, 6, 441) enable us to judge the reliability of the present method for determining the ignition point of inflammable gas mixtures. There can be no doubt that with the same arrangement the ignition temperature is sharp and entirely reproducible. Increment in the volume of the soap bubbles containing the inflammable mixtures, lowers the ignition point

up to a volume of 500 c.c. ; the ignition point remaining constant with larger volumes, a slight lag in the explosion being noticed. The influence of the composition is not so marked. The most important factor is the nature of the platinum surface. Experiments are, however, in progress to see if any additional information on this point is available. There is an important aspect of explosion which has been brought about by these experiments: the lowest ignition temperature is influenced by catalysis so considerably that the commonly accepted values of ignition temperatures of inflammable gas mixtures offer no indication of safety in technical accidents, where catalysing sources are frequent. Then the question of preflame period is important, as at considerably lower temperatures ignitions have been initiated through protracted warming. Incidentally, the production of H_2O_2 and O_3 in hydrogen oxygen explosions and a few conditions of their production have been investigated.

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Review

Elektrophorese, Elektroosmose, Elektrodialyse in Flüssigkeiten by P. H. Prausnitz, Dr.-Ing-in Jena, and J. Reitstötter, Dipl.-Ing., Dr. Phil., Dr. Techn. Published by Theodor Steinkopff, Dresden and Leipzig. Band XXIV. Royl 8vo., 307 pp.

This book constitutes the twenty fourth volume of the well-known series of publications edited by Dr. Raphael Ed. Liesegang, Frankfurt, a. M. The authors have very admirably collected an enormous amount of useful information which will be of advantage to students and specially to advanced workers on the subject. A special feature of the book is the information about Patent Literature and the industrial aspects of this rapidly developing branch of science. If the authors have not entered into a critical discussion of the theoretical aspects this is to be ascribed to the contradictory points of view characteristic of a subject in a formative stage of development. They have attempted to represent the different points of view as far as that is possible within the scope outlined for the book. The writer hopes that the book will be found useful.

J. N.M.

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists.—Third Edition, 1930.

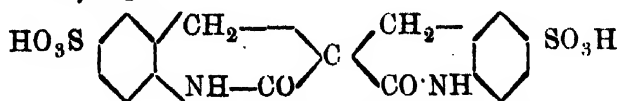
This edition is issued about six years after the publication of the second edition. There have been considerable additions, alterations and rearrangement of data in the new edition. The subject matter is broadly grounded into two divisions, non-foods *e.g.*, soils, fertilizers, liming materials, etc., and foods *e.g.*, baking powders, beverages, cereal products etc. A number of alternative methods of analysis are given on each subject and the technique of these analysis is brought up-to-date. A few new chapters have been added, dealing with caustic poisons, naval stores, paints, radio activity, eggs and egg products. Several related chapters have been combined into one so as to effect a certain amount of condensation in the text *e.g.*, the chapter on coffee has been combined with that on tea, gelatine with meat and meat products etc.

To those who are familiar with the first and the second editions the new edition will be a valuable supplement. As regards the general usefulness of a book of this kind it will suffice to say that for those engaged in analytical and research work in Agricultural chemistry, the new edition as a laboratory hand book is indispensable.

J. C. G.

ERRATA

Page	line	
3	6	<i>read</i> '(1592-1655)' <i>for</i> '(1592-1650)'
4	2	<i>delete</i> 'for' <i>after</i> 'accounted'
4		
4	37	<i>read</i> '1772' <i>for</i> '1722'
6	26	„ 'hold' <i>for</i> 'held'
7	5	„ '1844' <i>for</i> '184'
8	7	„ 'as he says' <i>for</i> 'he says'
9	21	<i>insert</i> full point in place of comma <i>after</i> extent
9	27	„ 'has' <i>for</i> 'had'
11	9	„ 'more' <i>for</i> 'mere'
14	13	<i>after</i> compounds, <i>insert</i> 'with identical reflected images and asymmetrical compounds'
15	26	<i>read</i> 'differ' <i>for</i> 'dlffer'
17	15	„ '382·4' <i>for</i> '382' and '-0·10' <i>for</i> '-0·14.'
18	4	<i>insert</i> 'structure and molecular' <i>before</i> configuration
18	38	<i>read</i> '1552' <i>for</i> '1542'
18	39	„ '116' <i>for</i> '115'
19	12	„ 'Boeseken' <i>for</i> 'Boesehen'
19	33	„ '18' <i>for</i> '23'
12	23	



for the formula given in the text.

Studies on Reimer-Tiemann Reaction.

By RAJENDRA NATH SEN AND SUSIL KUMAR RAY.

A systematic investigation of the Reimer-Tiemann reaction described in this communication, wherein the influence of the nature and position of substituents has been studied, has revealed that when chloroform (or carbon tetrachloride) is mixed with alcohol (1:3) the yield of the aldehyde (or the acid) is increased. It has also been found that in some cases where the sodium salt of the phenol is sparingly soluble *e.g.*, in the cases of *o*-bromophenol and 2-hydroxy-anthraquinone, the addition of a little pyridine to the alkali solution greatly helps the reaction, but however, the nitrophenols are not helped to an appreciable extent by this. It is interesting to note that aqueous pyridine may entirely replace alkali hydroxide solution; from phenol, salicylaldehyde being formed in this way in an yield of 10 per cent. whilst *p*-hydroxybenzaldehyde is not produced at all.

When Reimer-Tiemann's reaction is applied to *o*-coumaric acid, the entrant aldehyde-group attacks the *para* position only. Similar results are obtained also with 8-hydroxyquinoline where the *para* derivative is formed (30 per cent.) to a greater extent than the *ortho* (16 per cent.). *o*-Nitro- and bromophenols are converted into the corresponding aldehydes much better than the *para* analogues. Similarly *o*-bromophenol gives a better yield of the acid than the *para* compound with carbon tetrachloride.

The influence of negative substituents (NO_2 , Cl, Br and SO_3H) on the reaction is to inhibit the reaction as is to be expected, the nitro group exerting the maximum effect. This may also be partly due to the very sparing solubility of the alkali salts of nitrophenols and also to the specific inhibiting action of the nitro group, because negative groups like COOH (*cf.* aldehydosalicylic acid, yield 27 per cent., Wayne and Cohen, *J. Chem. Soc.*, 1922, 121, 1022), SO_3H (*cf.* aldehydophenol sulphonic acid, yield 21 per cent., *vide infra*) alone do not suppress the reaction to a very great extent.

The reaction has been successfully applied to thiophenol (yield 3.5 per cent., thiosalicylic acid with carbon tetrachloride), 2-hydroxy-

anthraquinone (yield 25 per cent. of the *ortho*-aldehyde), 8-hydroxyquinoline (yield 16 per cent. of *ortho* and 30 per cent. *para* aldehydes) and to thymol which gives 17 per cent. of *ortho*- and 11 per cent. of *para*-aldehydes.

The new aldehydes described in this paper condense to give interesting dyes which will be described subsequently.

EXPERIMENTAL.

Salicylaldehyde and p-hydroxybenzaldehyde.—When a mixture of phenol (50 g.), chloroform (50 c.c.) and alcohol (150 c.c.) was stirred into a solution of sodium hydroxide (100 g. in 160 c.c. water) at 60° for 4 hours, gave 18 g. of salicylaldehyde and 3.5 g. of *p*-hydroxybenzaldehyde, after working up in the usual way.

A mixture of chloroform (15 c.c.) and alcohol (45 c.c.) and a solution of phenol (15 g.) in aqueous pyridine (50 g. in 30 c.c. water) when heated at 100° for 30 hours gave 2 g. of salicylaldehyde.

Salicylic acid and p-hydroxybenzoic acid.—By heating phenol (50 g.) carbon tetrachloride (85 g.), alcohol (200 c.c.) and caustic soda solution (110 g. in 176 g. water) for 36 hours, 7.3 g. of salicylic acid and 2 g. of *p*-hydroxybenzoic acid were formed. The yield was only 5 p.c. without using alcohol.

3-Nitrosalicylaldehyde.—A solution of nitrophenol (50 g.), chloroform (36 c.c.) and alcohol (120 c.c.) was added drop by drop to caustic soda solution (62 g. in 100 c.c. water and heated on a water-bath for 8 hours. The brownish mass separated on acidification with hydrochloric acid, was washed with water and finally crystallised from alcohol, m.p. 109°, yield 5.4 g. It was found identical with the compound prepared by nitration of salicylaldehyde (Miller, *Ber.*, 1887, 20, 1928). (Found: N, 8.42. $C_7H_5O_4N$ requires N, 8.38 per cent.). It forms a monoacetyl derivative (m.p. 150°) identical with the acetyl derivative of 3-nitrosalicylaldehyde of Miller (*loc. cit.*).

2-Nitro-4-hydroxybenzaldehyde was prepared from 3-nitrophenol exactly as in the previous case. The aldehyde was separated by dissolving in hot benzene, in which it is more soluble than 3-nitrophenol. It was finally crystallised from water, m.p. 67°, yield 1.2 g. from 50 g. of *m*-nitrophenol. It was found identical with the aldehyde and its phenylhydrazone (m.p. 189°) prepared by Sachs and Kantorowicz (*Ber.*, 1906, 39, 2754).

5-Nitrosalicylaldehyde was prepared from *p*-nitrophenol, and purified through the bisulphite compound, the yield being 3 g. from 30 g. of *p*-nitrophenol. It was found identical with the aldehyde prepared by Miller (*loc. cit.*).

3-Bromosalicylaldehyde and 3-bromo-*p*-hydroxybenzaldehyde were prepared from *o*-bromophenol (25 g.) chloroform (15 c.c.), alcohol (50 c.c.) and sodium hydroxide solution (27.5 g. in 50 c.c. water). The temperature was kept at 50-60° initially for 3 hours and the mixture was then heated on the boiling water-bath for 6 hours. The thick red oil, separating on acidification, was distilled in steam and the *o*-aldehyde crystallised from dilute alcohol in pale yellow crystals, m.p. 52°, identical with the aldehyde prepared by Müller (*Ber.*, 1909, 42, 695) by reduction of 3-nitrosalicylaldehyde and then by diazo-reaction. Yield 3.8 g. The aldehyde forms a semicarbazone (m.p. 266°) identical with the semicarbazone of the aldehyde prepared by Müller.

The mother-liquor from which the *o*-compound had been removed, was treated several times with boiling water to extract the *p*-aldehyde. The aqueous extract on cooling, deposited colourless crystals of 3-bromo-*p*-hydroxybenzaldehyde, which was further crystallised from chloroform, m.p. 124°, yield 1 g. It was found identical with the aldehyde prepared by bromination of salicylaldehyde (Hantzsch and Mai, *Ber.*, 1895, 28, 2469).

The semicarbazone crystallised from alcohol in almost colourless needles, m.p. 195-96°. (Found: N, 16.45. $C_8H_8O_2N_3Br$ requires N, 16.28 per cent.).

If in the above reaction pyridine (15 c.c.) be added to the alkali, the yields of the *o*- and *p*-aldehydes increase to 5 g. and 1.5 g. respectively.

5-Bromosalicylaldehyde was prepared from 5-bromophenol and purified through the bisulphite compound, m.p. 104°, yield 2.5 g. It was found identical with the compound prepared by bromination of salicylaldehyde (Henry, *Ber.*, 1869, 2, 275; *ibid.*, 1889, 22, 1135; Auwers and Walker, *ibid.*, 1898, 31, 3042; Auwers and Burger, *ibid.*, 1904, 37, 3934).

The semicarbazone crystallised from alcohol in colourless needles decomposing at 297°. (Found: N, 16.6. $C_8H_8O_2N_3Br$ requires N, 16.3 per cent.).

3-Bromo- and 5-bromosalicylic acids were prepared from *o*- and *p*-bromophenols respectively. A mixture of *o*-bromophenol

(2.5 g.), carbon tetrachloride (17 c.c.), alcohol (50 c.c.) and caustic soda solution (86.5 g. in 73 g. water) was heated for 12 hours on the water-bath. The acids were isolated from their barium salts by acidification.

3-Bromosalicylic acid was found identical with the compound prepared from 3-bromo-5-aminosalicylic acid (Lellmann and Grothmann, *Ber.*, 1884, 17, 2715); it crystallises from 50 per cent. methyl alcohol, m.p. 184°, yield 0.5 g. The barium salt crystallises in red prisms from hot water (*cf.* Meldrum and Shah, *J. Chem. Soc.*, 1923, 123, 1986). [Found: Ba, 21.68; H₂O, 9.12. (C₇H₄O₃Br)₂Ba, 3H₂O requires Ba, 21.99; H₂O, 8.66 per cent.].

5-Bromosalicylic acid crystallises from boiling water, m.p. 164-65°, yield 0.3 g. It was found identical with the compound prepared by the action of phosphorus tribromide on salicylic acid (Henry, *loc. cit.*; Hand, *Annalen*, 1886, 234, 133; 1893, 273, 122). (Found: Br, 36.97. C₇H₅O₃Br requires Br, 36.8 per cent.).

5-Chlorosalicylaldehyde was prepared from *p*-chlorophenol as in the preparation of 3-bromosalicylaldehyde. It was purified through the bisulphite derivative and found identical with the compound prepared from salicylaldehyde (Biltz and Stept, *Ber.*, 1904, 37, 4024; Piria, *Annalen*, 1851, 80, 196), m.p. 99.5°, yield 0.9 g. from 25 g. phenol. The semicarbazone melts at 286-87° and was found identical with the semicarbazone of the aldehyde prepared by Biltz and Stept. (*loc. cit.*).

5-Chlorosalicylic acid, identical with the compound prepared by Beilstein (*Ber.*, 1875, 8, 816) was prepared from *p*-chlorophenol (25 g.) carbon tetrachloride (200 c.c.) and caustic soda solution (45 g. in 90 c.c. water). The acid crystallises from hot water, m.p. 167.5°, yield 0.2 g.

1-Aldehydo-2-hydroxybenzene-3-sulphonic acid was prepared from phenol-*o*-sulphonic acid (10 g.) chloroform (10 c.c.), alcohol (35 c.c.) and caustic soda solution (20 g. in 32 c.c. water). The aldehyde crystallises from hot water in golden yellow needles. It is soluble in hot water, sparingly soluble in alcohol, insoluble in ether, chloroform acetone and benzene; it does not melt below 250°. (Found: S, 16.00. C₇H₆O₅ S requires, S, 15.84 per cent.).

5-Aldehydo-*o*-coumaric acid, CHO·C₆H₃·OH (CH:CH·COOH) (5:2:1).—A solution of *o*-coumaric acid (15 g.) and chloroform (14.5 g.) in alcohol (30 c.c.) was added to a solution of caustic soda (28 g. in 80 c.c. water) as in the preparation of 3-bromosalicylaldehyde.

hyde, but the heating was continued for 12 hours. The brick-red powder, separated on acidification, was filtered hot. The aldehyde separated from the filter on cooling, and was crystallised from dilute alcohol in pale yellow microcrystalline needles, m.p. 220° (decomp.), yield 1.8 g. It is described identical with the aldehyde by Sen and Chakravarti (*J. Indian Chem. Soc.*, 1930, 7, 249). (Found: C, 62.41; H, 4.20. $C_{10}H_8O_4$ requires C, 62.50; H, 4.16 per cent.).

The silver salt was prepared in the usual way as yellow powder. (Found: Ag, 36.3. $C_{10}H_7O_4Ag$ requires Ag, 36.1 per cent.).

The phenylhydrazone, prepared in the usual way, crystallised from dilute acetic acid as a yellow microcrystalline powder, m.p. 236° (decomp.). (Found: N, 10.22. $C_{16}H_{14}O_3N$ requires N, 9.92 per cent.).

The semicarbazone prepared in the usual way, crystallised from dilute alcohol in almost colourless microcrystalline powder, m.p. 275° . (Found: N, 16.7. $C_{11}H_{11}O_4N_3$ requires N, 16.86 per cent.).

6-Aldehydocoumarin.—5-Aldehydo-*o*-coumaric acid (2 g.) was dissolved in the least quantity of concentrated sulphuric acid and heated on the water-bath for 2 hours. When poured into water, it deposited a brown mass, which was filtered, treated with sodium carbonate solution to remove the unchanged 5-aldehydo-*o*-coumaric acid. It crystallised from alcohol, m.p. $187-89^{\circ}$. It was found identical with the aldehyde prepared by Stoermer and Oetker (*Ber.*, 1904, 37, 192) and Sen and Chakravarti (*J. Amer. Chem. Soc.*, 1928, 50, 2428).

5-Carboxyl-*o*-coumaric acid, $COOH \cdot C_6H_3 \cdot OH$ ($CH:CH:COOH$) (5:2:1).—*o*-Coumaric acid (15 g.) and carbon tetrachloride (17 g.) dissolved in alcohol (35 c.c.) was added drop by drop to caustic soda solution (26.5 g. in 42.5 g. water) and the solution heated on the water-bath for 20 hours with vigorous stirring. The separation of the dicarboxylic acid was effected as in the case of 5-aldehydo-*o*-coumaric acid. It crystallised from alcohol in pale yellow needles, decomposing at 186° and finally melting at 210° , yield 0.5 g. It is soluble in hot water, hot alcohol, and acetone; sparingly soluble in cold alcohol; insoluble in ether, chloroform and benzene. It gives reddish colour with ferric chloride.

Di-silver salt was prepared in the usual way from ammonium salt as yellow powder. (Found: Ag, 51.28. $C_{10}H_6O_5Ag_2$ requires Ag, 51.18 per cent.).

2-Methyl-5-isopropyl-6-hydroxybenzaldehyde.—A solution of thymol (15 g.) and chloroform (16 g.) in alcohol (90 c.c.) was added drop

by drop to caustic soda solution (20.5 g. in 38 c.c. water) and the whole heated on the water-bath to 30° to start the reaction. The stirring was continued for 5 hours at the room temperature. The deep red oil, separating on acidification, was submitted to distillation with steam when the *o*-compound separated as a pale yellow oil. This was taken up with ether and purified through the bisulphite compound, *b. p.* 233°, yield 3 g. It is insoluble in water and soluble in alcohol, ether, chloroform and petroleum ether; gives an intense violet coloration with ferric chloride. (Found: C, 74.00; H, 8.01. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.86 per cent.).

The *semicarbazone*, prepared in the usual way crystallised from alcohol as colourless tiny needles, *m.p.* 242°. (Found: N, 18.10. $C_{12}H_{17}O_2N_3$ requires N, 17.86 per cent.).

6-Methyl-3-isopropyl-4-hydroxybenzaldehyde.—After the removal of *o*-aldehyde with steam, the non-volatile *p*-compound remained as a brownish-red substance. The aqueous portion was filtered hot, the residue dissolved in caustic soda and precipitated by neutralising with acetic acid. The process was repeated four or five times. The aldehyde was crystallised from dilute alcohol in brownish needles, *m.p.* 108–10°, yield 2 g. It is insoluble in water and petroleum ether; easily soluble in alcohol, ether and chloroform; it gives no coloration with ferric chloride. (Found: C, 73.77; H, 8.21. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.85 per cent.).

The *semicarbazone* crystallised from alcohol as pale yellow needles, *m.p.* 191°. (Found: N, 18.03. $C_{12}H_{17}O_2N_3$ requires N, 17.86 per cent.).

7-Aldehyde-8-hydroxyquinoline.—A mixture of 8-hydroxyquinoline (15 g.), chloroform (14 g.), alcohol (60 c.c.) and sodium hydroxide solution (16.5 g. in 28 c.c. water) was heated at 100° for 12 hours. Alcohol and the excess of chloroform were driven off. The solution was made just acidic with hydrochloric acid when a brick-red powder separated which was washed first with ether to remove the unchanged hydroxyquinoline and then with chloroform. The chloroform solution furnished the 7-aldehyde-8-hydroxyquinoline which crystallised from a mixture of chloroform and alcohol in reddish microcrystalline powder melting above 250°, yield 3 g. It is insoluble in water, alcohol, acetone, carbon tetrachloride and benzene; easily soluble in chloroform, pyridine, quinoline, and acetic acid; it gives a greenish yellow coloration with ferric chloride. (Found: N, 8.15. $C_{10}H_7O_2N$ requires N, 8.09 per cent.).

5-Aldehydo-8-hydroxyquinoline.—The residue left after removal of the *ortho*-compound with chloroform crystallised from boiling quinoline as brownish powder, melting above 250° , yield 5.5 g. It is insoluble in water, ether, chloroform, carbon tetrachloride, acetone, benzene and alcohol; soluble with difficulty in nitrobenzene and quinoline; easily soluble in acetic acid and pyridine; gives no coloration with ferric chloride. (Found: N, 8.22. $C_{10}H_7O_2N$ requires N, 8.09 per cent.).

1-Aldehydo-2-hydroxyanthraquinone.—A solution of 2-hydroxyanthraquinone (10 g.) and chloroform (10 c.c.) in alcohol (60 c.c.) was added to caustic soda solution (10 g. in 16 c.c. water) and heated on the water-bath for 30 hours. The olive-brown mass, separating on acidification, was washed with hot water and dried; the unchanged 2-hydroxyanthraquinone was removed with boiling nitrobenzene; the aldehyde was washed with petroleum ether. It can be crystallised from a very large excess of boiling nitrobenzene as yellowish powder melting above 300° , yield 1.8 g. It is insoluble in all ordinary organic solvents; soluble with difficulty in boiling carbon disulphide and boiling nitrobenzene; easily soluble in pyridine. (Found: C, 71.23; H, 3.17. $C_{15}H_8O_4$ requires C, 71.42; H, 3.17 per cent.).

Thiosalicylic acid.—A solution of carbon tetrachloride (11 c.c.) in alcohol (30 c.c.) was added to a mixture of thiophenol (14 g.) and sodium hydroxide solution (23 g. in 33 c.c. water) and the mixture heated for 30 hours on the water-bath. On acidification, a little pale yellow mass separated out; the unchanged thiophenol was distilled off with steam; the solid residue filtered, washed with water and crystallised from alcohol, m.p. 163° , yield 0.5 g. It was found identical with the compound prepared from *o*-chlorobenzoate and potassium hydrosulphide (D.R.P. 189200). (Found: S, 20.92. $C_7H_6O_2S$ requires S, 20.77 per cent.).

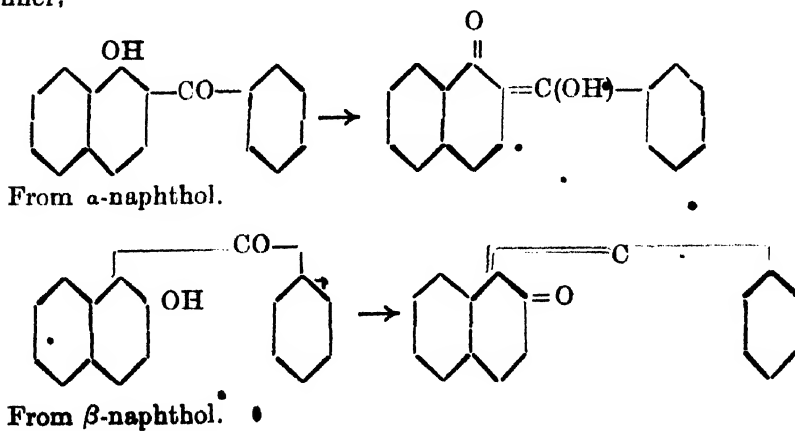
Condensation of Benzotrichloride with Phenols.

BY RAJENDRA NATH SEN AND SUSIL KUMAR RAY.

Benzoylphenol or oxybenzophenone was previously obtained by Doebner and Stockmann (*Ber.*, 1877, 10, 1969) together with phenylbenzoate and benzyolphenol-benzoate by the action of benzotrichloride on a mixture of phenol and zinc oxide.

Heiber (*Ber.*, 1891, 24, 3677) obtained in a very poor yield (about 1 p. c.) *o*-hydroxybenzophenone by heating a mixture of phenol, benzotrichloride and caustic soda. It has now been found that an alcoholic solution of benzotrichloride (3:1) reacts more satisfactorily with an alkaline solution of phenol at the temperature of the boiling water-bath yielding about 5 p. c. *ortho*-hydroxybenzophenone. The nitrophenols appear not to react with benzotrichloride. The naphthols, however, react more readily with benzotrichloride. With α -naphthol two products are obtained, one soluble in alkali (yield 4 p.c.), reacts with phenylhydrazine and semicarbazide, while the other (yield 16 p. c.) is insoluble in alkali and does not react with phenylhydrazine and semicarbazide. The β -naphthol compound (yield 20 p. c.) also is insoluble in alkali and behaves similarly.

It is concluded that the compound soluble in alkali is the *p*-hydroxynaphthylphenylketone, while the alkali insoluble products are the *o*-compounds undergoing tautomerisation in the following manner,



which explains the insolubility of the compounds in alkali, and also their inactivity towards phenylhydrazine and semicarbazide, probably due to the steric hindrance as suggested by Kehrman (*Ber.*, 1888, **21**, 3315 ; 1890, **23**, 3557).

It is interesting to note that *o*-coumaric acid reacts readily with benzotrichloride, forming the corresponding ketone, *p*-coumaryl-phenylketone (yield 30 p. c.). The compound is presumably the *p*-derivative, as the *o*-substitution product is not ordinarily formed in the case of *o*-coumaric acid.

EXPERIMENTAL.

o-Hydroxybenzophenone.—A mixture of phenol (30 g.) and benzotrichloride (4 g.) dissolved in alcohol (140 c. c.) was added drop by drop to a solution of caustic soda (55 g. in 90 c. c. water) with constant stirring. The mixture was heated on the boiling water-bath for 8 hours. On acidification a reddish-brown semi-solid mass separated out, which was washed several times with hot water. The dried mass was next washed with petroleum ether to remove the excess of benzotrichloride. It was then dissolved in caustic soda. The alkaline solution cooled to 0° and was then neutralised with acetic acid. The yellowish mass was filtered and the process repeated several times, until a pale yellow solid was obtained. It was finally crystallised from dilute alcohol as pale yellow needles, m. p. 41°, yield 3 g. It was found identical with the compound prepared by Heiber (*loc. cit.*) in an yield of 3.5 g. from 144 g. of phenol.

The *oxime*, obtained by the usual method, crystallised in needles, m. p. 132-133°. It was found identical with the *oxime* (m. p. 133°) prepared by Heiber (*loc. cit.*).

o- & *p*-Hydroxynaphthylphenylketones.—A solution of α -naphthol (10 g.), benzotrichloride (17 g.) and alcohol (40 c. c.) was added to a solution of caustic soda (15 g. in 30 c. c. water) as in the preceding compound. But the temperature was kept between 50-60°. The product, separating on acidification, was washed with water and then with petroleum ether. It was then treated with ammonia to remove the *p*-compound. The *o*-compound was crystallised from boiling chloroform in brownish microcrystalline powder, m. p. 114°, yield 3 g. It is insoluble in water, ether, petroleum ether and ammonia ; sparingly soluble in alcohol, chloroform, benzene and boiling caustic soda ; easily soluble in acetone. It gives no

coloration with ferric chloride. (Found: C, 82.40; H, 5.21. $C_{17}H_{12}O_2$ requires C, 82.26; H, 4.83 per cent.).

The ammoniacal solution containing the *p*-compound when acidified with acetic acid, yielded a brick-red powder which was crystallised from very dilute alcohol, m. p. 162-64°, yield 1 g. It is easily soluble in alcohol, ether, chloroform and acetone; insoluble in water, benzene and petroleum ether. It gives a greenish orange coloration with ferric chloride. It was found identical with the compound (m. p. 164-65°) prepared from 1-hydroxy-naphthyl 2-carboxylic acid and benzotrichloride without any alkali (D. R. P., 378908, 378909; Swiss Pat., 98559). (Found: C, 82.1; H, 4.64. $C_{17}H_{12}O_2$ requires C, 82.25; H, 4.83 per cent.).

2-Hydroxy- α -naphthylphenylketone.—The reaction was carried out with β -naphthol, benzotrichloride, alcohol and alkali as in the first compound. The product, separating on acidification was washed with alkali and finally with water. It was crystallised from a mixture of alcohol and chloroform as a brick-red microcrystalline powder, m. p. 174°, yield 5 g. It is insoluble in water, cold alkali, alcohol and petroleum ether; soluble with difficulty in ether and boiling caustic soda; easily soluble in chloroform, acetone and benzene; does not give any coloration with ferric chloride. It was found identical with the compound prepared from β -naphthol and benzotrichloride without any alkali (D. R. P., 378908, 378909; Swiss Pat., 98559). (Found: C, 82.51; H, 5.31. $C_{17}H_{12}O_2$ requires C, 82.25; H, 4.83 per cent.).

o-Coumarylphenylketone.—A solution of *o*-coumaric acid (15 g.), benzotrichloride (20 g.) and alcohol (100 c. c.) was added to a solution of caustic soda (25 g. in 41 c. c. water) as in the first compound. The heating and stirring were continued for 12 hours. On acidification, a black tarry liquid separated out which was washed with petroleum ether to remove the excess of benzotrichloride. The product was dissolved in alkali and reprecipitated with acetic acid. The process was repeated for several times, until a brownish solid was obtained, which was next boiled with water to remove the unchanged *o*-coumaric acid. The mixture was filtered hot and the residue crystallised from dilute alcohol in yellowish microcrystalline powder, m. p. 188°, yield 7.2 g. It is insoluble in water, chloroform and petroleum ether; moderately soluble in alcohol and easily soluble in ether. (Found: C, 71.78; H, 4.57. $C_{16}H_{12}O_4$ requires C, 71.64; H, 4.47 per cent.).

Silver salt was prepared in the usual way from ammonium salt as yellow powder. (Found: Ag, 28·77. $C_{16}H_{11}O_4$ Ag requires Ag, 28·80 per cent.).

The *phenylhydrazone*, prepared in the usual way, crystallised from alcohol as reddish tiny needles, m. p. 120° (decomp.). (Found: N, 7·7. $C_{22}H_{18}O_3N_2$ requires N, 7·8 per cent.).

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Mercuration of Compounds containing the Reactive Methylene ($-\text{CH}_2-$) group by means of Mercuric Acetate.

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The mercuration of the substituted amides of acetoacetic acid and malonic acid was undertaken with a view to study the formation and the properties of the organo-mercury derivatives of compounds containing a reactive methylene group, and throw light, if possible, on the reactivity of the hydrogen atoms of a reactive methylene ($-\text{CH}_2-$) group, situated between two carbonyl groups.

With this end in view, mercuric acetate was allowed to react in methyl alcohol with the following substances :

(1) Acetoacetanilide, (2) acetoacet-*o*-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet-*p*-toluidide, (5) acetoacet- α -naphthylamide, (6) acetoacet- β -naphthylamide, (7) acetoacet-1:3:4-xylidide, (8) acetoacet-1:4:5-xylidide, (9) ethyl acetoacetate, (10) acetoacet-*m*-nitranilide, (11) ethyl malonate, (12) malonmonophenylamide, (13) malonmono-*o*-toluidide, (14) malonmono-*m*-toluidide, (15) malonmono-*p*-toluidide, (16) malonmono- α -naphthylamide, (17) malonmono- β -naphthylamide, (18) malonmono-1:3:4-xylidide, (19) malonmono-1:4:5-xylidide and (20) malonamide.

Of these (18) and (19) were prepared for the first time by the modification of Whiteley's method (*J. Chem. Soc.*, 1903, 83, 24).

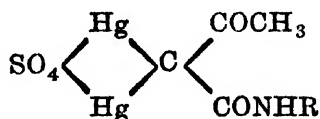
It has been found that when mercuric acetate reacts with aromatic compounds, it introduces very easily the acetoxymcury ($\text{CH}_3\text{-COOHg-}$) group in the nucleus. It was, therefore, expected that in these reactions also, it would not only attack the methylene group, but also attack the aromatic part of these amides. Contrary to our expectations, it was found that mercuric acetate attacked the methylene group only, leaving the aromatic nucleus unaffected, even when mercuric acetate was employed in excess.

Whereas, the amides (1—11) reacted with mercuric acetate in methyl alcohol giving diacetoxymcury derivatives of the formula

removed by dilute hydrochloric acid, potassium iodide and hydrogen sulphide (*cf.* Schrauth and Bauerschmidt, *Ber.*, 1914, **47**, 2740), while the mercury in these compounds is easily removed.

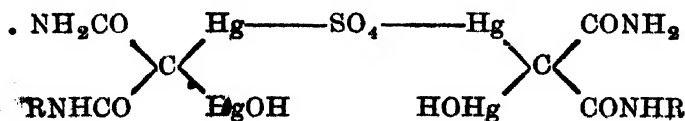
(iv) That the substituted grouping containing mercury is directly attached to the carbon atom of the methylene group, situated between two carbonyl groups, for, (a) the properties and the behaviour of compounds described here, are exactly similar to those having mercury attached to a carbon atom in α -position to a carbonyl group. It has been observed in case of mercurated 5-pyrazolone (which contains four acetoxymercury groups) that the mercury in position-4 (*i.e.*, attached to a carbon atom in α -position to a carbonyl group in position-5) is easily removed by dilute hydrochloric acid and hydrogen sulphide, the other three acetoxymercury groups, keeping firmly to their positions in the molecule, (Schrauth and Bauerschmidt, *loc. cit.*). (b) On bromination of acetoxymercurimalonamide, dibromomaltonamide is obtained.

Mercury compounds of the type (I) react with 10 p.c. sulphuric acid giving compounds of the following constitution:



They also react with an aqueous solution of potassium iodide with the separation of the original amide and the liberation of potassium hydroxide. The potassium hydroxide, liberated was found to be 2.018 equivalents, which according to theory should be 2 equivalents. These facts completely prove the constitution assigned to the compounds of the type (I).

Mercury compounds of the type (II), react with standard sodium hydroxide solution, giving a dihydroxymercury derivative. The quantity of sodium hydroxide required to completely hydrolyse the acetoxymercury ($-\text{CH}_3\text{COOHg}-$) group was found to be 1.12 equivalents which according to theory should be .1 equivalent. The constitution is further supported by the behaviour of the compounds with sulphuric acid. They give rise to hydroxysulphatomercury derivatives of the following constitution.



When hydroxyacetoxymercuri-*o*-toluidide is, however, made to react with an aqueous solution of potassium iodide, 2·97 equivalents of potassium hydroxide are liberated, which according to the theory should be 3 equivalents. This lends a further strong support to the correctness of the constitution assigned.

EXPERIMENTAL.

Diacetoxymercuriacetoacetanilide.—Mercuric acetate (3·6 g.) dissolved in methyl alcohol, was added to a methyl alcohol solution of acetoacetanilide (1 g.). The solution though clear at first became turbid on heating on a sand-bath for about 10 minutes. On cooling, a snow white crystalline product separated out. It was filtered and washed with water, alcohol and ether to remove the unreacted constituents. The product was insoluble in most of the ordinary organic solvents. It melts with decomposition at 204°. (Found: N, 2·23; Hg, 57·26. $C_{14}H_{15}O_6NHg_2$ requires N, 2·02; Hg, 57·72 per cent.).

The rest of the mercury derivatives have been similarly prepared by the interaction of mercuric acetate with the respective amides in methyl alcohol. The results are given in Table I.

Action of dilute hydrochloric acid.—The above mercury compound decomposed by hot 0·25N-hydrochloric acid with the separation of the original amide and mercuric chloride.

Action of potassium iodide.—The above compound (0·2627 g.) suspended in water, was treated with a solution of potassium iodide (1g.). Potassium hydroxide was at once liberated and titrated against 0·0574N-hydrochloric acid (of which 13·3 c.c. were required). It was subsequently heated for about 1 hour, but no further liberation of potassium hydroxide was observed.

Action of hydrogen sulphide.—The above mercury compound (0·491 g.) was suspended in water and heated to boiling. A slow current of hydrogen sulphide gas was passed into the solution till the complete precipitation of mercuric sulphide. Precipitates were then filtered through a Gooch crucible and washed with water, pyridine, carbon disulphide and alcohol to remove the amide formed during the course of the reaction as well as the sulphur which might have precipitated together with mercuric sulphide. It was then dried at 105-10°, and weighed (0·83 g.). (Found: Hg, 57·9. $C_{14}H_{15}O_6NHg_2$ requires Hg, 57·72 per cent.).

This indicated that the splitting up of the carbon—mercury linkage by hydrogen sulphide was quantitative.

Action of phenylhydrazine.—The substance decomposed on treatment with phenylhydrazine with the separation of grey metallic mercury.

Sulphatomercuriacetoacetanilide.—The above mercury compound (2 g.) was heated with 10 p. c. sulphuric acid on sand-bath for about $\frac{1}{2}$ hour. It was then cooled, filtered and washed with water, alcohol and ether. The product was insoluble in most of the ordinary organic solvents. It turned brown at 240° but did not melt till 300° . (Found: Hg, 59.20 ; SO_4 , 14.55. $\text{C}_{10}\text{H}_9\text{O}_6\text{NSHg}_2$ requires Hg, 59.61 ; SO_4 , 14.3 per cent.).

Compounds similar to the above have been prepared by the action of sulphuric acid on compounds 1,2,3,9,12, and 20 of Table I.

The results are given in Table II. Compounds are numbered as 1a, 2a, 3a, 9a, 12a, and 20a.

Action of potassium iodide on diacetoxymercuriacetoacet-o-toluidide.—Diacetoxymercuriacetoacet-o-toluidide (1 g.) was treated with potassium iodide in water and heated to boiling. The liberated alkali was neutralised and the solution concentrated and cooled when crystalline needles of acetoacet-o-toluidide separated, m.p. 107° .

Action of dilute sodium hydroxide on acetoxyhydroxymercurimalonmonophenylamide.—The mercury compound (0.5038 g.) was treated with 50 c. c. of 0.018N-sodium hydroxide solution and refluxed for $\frac{1}{2}$ hour. It was cooled, filtered and washed with water. The filtrate was then acidified with 10 c.c. of 0.1N-oxalic acid to neutralise the unreacted sodium hydroxide. The excess of oxalic acid was titrated against 0.018 N-sodium hydroxide (55 c.c.).

The insoluble product was found to be dihydroxymercurimalonmonophenylamide. (Found: Hg, 65.1. $\text{C}_9\text{H}_{10}\text{O}_4\text{N}_2\text{Hg}_2$ requires Hg, 65.57 per cent.).

Action of potassium iodide on Acetoxyhydroxymercurimalonmono-o-toluidide.—Acetoxyhydroxymercurimalonmono-o-toluidide (0.2127 g.) was treated with potassium iodide (1 g.) in water and boiled for 4 hours. The liberated alkali was neutralised by 0.0574 N-hydrochloric acid (16.5 c.c.).

Malonmono-1:3:4-xylylidide.—This was prepared by the modification of Whiteley's method (*loc. cit.*). Ethyl malonate (80 g.) and 1:3:4-xylylidide (15 g.) were put in a flask, fitted with a cork

through which passed a long bent tube and heated in paraffin-bath, at 120-25°. To get the maximum yield, the temperature was not allowed to go beyond 125°. After 8 hours, the contents of the flask were transferred to a glass-stoppered bottle and shaken for 4 hours with twice its volume of ammonia ($d\ 0.88$). The semi-solid mass was then allowed to evaporate and the residue was pressed on a filter and finally washed with ether to remove any of the unreacted ester and amine. It was then boiled with dilute alcohol (1:6) and filtered hot. The dixylidide and xylylamate remained on the filter undissolved. The filtrate on cooling separated malonmono-1:3:4-xylyl-ide. The product when crystallised from the same solvent melts at 166°.

It is very soluble in methyl alcohol, ethyl alcohol, acetic acid, hot water, and sparingly soluble in cold water, hot benzene, but practically insoluble in petroleum. (Found: N, 13.57. $C_{11}H_{14}O_2N_2$ requires N, 13.59 per cent.).

Malonmono-1:4:5-xylyl-ide.—1:4:5-Xylidine (15 g.) and ethyl malonate (30 g.) were heated similarly for 8 hours at 120-25° as usual and subsequently treated as the preceding compound. It was crystallised from dilute alcohol (1:6), m.p. 197°. Solubility is similar to that of the preceding compound. (Found: N, 13.57. $C_{11}H_{14}O_2N_2$ requires N, 13.59 per cent.).

Action of bromine on acetoxyhydroxymercurimalonamide.—The mercury compound of malonamide was treated with an aqueous solution of bromine till no more bromine was absorbed. It was then heated to boiling when all the compound went in solution. The solution on cooling deposited a crystalline product which when filtered and washed with alcohol, melts at 203°. This was identical with the dibromomalonamide obtained by Freund (*Ber.*, 1884, 17, 782).

TABLE I.

(A = Acetoxyhydroxymercuroimalon-*, D = diacetoxymercuroacetoacet-.)

No.	Name.	Formula.	Colour changes.	M.p.	Analysis
					Found. Calc.
1.	D-anilide	$C_{14}H_{15}O_6NHg_2$	204° (decomp.)	Hg, 57.26 N, 2.23 57.73 p. c. 2.02
2.	D-o-toluidide	$C_{15}H_{17}O_6NHg_2$	184°	Hg, 56.12 N, 2.07 56.57 1.98
3.	D-m-toluidide	$C_{15}H_{17}O_6NHg_2$	194° (decomp.)	Hg, 56.21 56.57
4.	D-p-toluidide	$C_{15}H_{17}O_6NHg_2$	181°-82°	Hg, 56.96 56.57
5.	D-α-naphthylamide	$C_{18}H_{17}O_6NHg_2$	200° (decomp.)	Hg, 53.6 53.83
6.	D-β- do	$C_{18}H_{17}O_6NHg_2$	197°	Hg, 53.4 53.83
7.	D-1:3:4-xylylide	$C_{16}H_{19}O_6NHg_2$	192°	Hg, 55.01 55.48
8.	D-1:4:5-xylylide	$C_{16}H_{19}O_6NHg_2$	204°	Hg, 55.00 55.48
9.	Ethyl-diacetoxymercuro-acetoacetate	$C_{10}H_{14}O_7Hg_2$	Yellow and then reddish brown liquid at 270°	does not melt till 300° decomp. above 200°	Hg, 61.7 61.9
10.	D-m-nitranilide	$C_{14}H_{14}O_8N_2Hg_2$	Hg, 54.44 54.2
11.	Ethyl-diacetoxymercuro-malonate	$C_{11}H_{16}O_8Hg_2$	does not melt till 300° (decomp.)	Hg, 58.6 59.16
12.	A-monophenylamide	$C_{11}H_{15}N_2O_8Hg_2$	Turns yellow above 250°	" " decomp. till 300°	Hg, 60.9 61.35
13.	A-mono-o-toluidide	$C_{12}H_{14}O_8N_2Hg_2$	decomposes above 270°	Hg, 59.91 60.00 N, 4.09 4.2
14.	A-mono-m-toluidide	$C_{12}H_{14}O_8N_2Hg_2$	Yellow above 90° Brown at 290°	does not melt till 300°	Hg, 59.68 60.06
15.	A-mono-p-toluidide	$C_{12}H_{14}O_8N_2Hg_2$	Reddish brown above 280°	Hg, 59.90 60.00
16.	A-mono-α-naphthylamide	$C_{15}H_{14}O_8N_2Hg_2$	274° (decomp.)	Hg, 56.54 56.28
17.	A-mono-β-naphthylamide	$C_{15}H_{14}O_8N_2Hg_2$	275° (decomp.)	Hg, 57.4 56.98
18.	A-mono-1:3:4-xylylide	$C_{13}H_{16}O_8N_2Hg_2$	Yellow above 250°	270° (decomp.)	Hg, 58.35 58.82
19.	A-mono-1:4:5-xylylide	$C_{13}H_{16}O_8N_2Hg_2$	Yellow above 280 and Brown at 275°	Hg, 59.04 58.82
20.	A-amide*	$C_3H_6O_3N_2Hg_2$	does not mel till 390°	Hg, 69.9 69.44

TABLE II.

(S = Sulphatomercuri-acetoact).

No.	Name.	Formula.	Colour change.	M.p.	Analysis.	
					Found.	Calc.
1a.	S-anilide	$C_{10}H_9O_6NSHg_2$	Brown at 240°	Did not melt till 300°	Hg, 59.2 SO_4 , 14.55	59.61 p.c. 14.30
2a.	S-o-toluidide	$C_{11}H_{11}O_6NSHg_2$	Brown above 240°	SO_4 , 14.25	14.01
3a.	S-p- do	$C_{11}H_{11}O_6NSHg_2$	Brown above 250°	Did not melt till 300°	SO_4 , 14.6	14.01
9a.	Ethyl sulphatomercuriacetoacetate	$C_8H_9O_7SHg_2$	Yellow above 200°, reddish brown at 230°	SO_4 , 14.7	15.3
12a.	Hydroxysulphatomercuri-malon-mono-phenylamide	$C_{18}H_{18}O_{10}N_4SHg_4$	Yellow above 250° brown at 265°	Hg, 62.53 SO_4 , 8.1	62.4 7.49
20a.	Hydroxysulphatō-mercury-malonamide	$C_6H_{10}O_{10}N_4SHg_4$	does not decompose till 300°	Hg, 70.4 SO_4 , 7.9	70.8 8.49

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Influence of Temperature on the Setting of Inorganic Jellies.

BY SATYA PRAKASH.

In previous publications from this laboratory (*J. Indian Chem. Soc.*, 1929, **6**, 391, 587; *ibid*, 1930, **7**, 367, 417, 591; *Z. anorg. Chem.*, 1931, **201**, 301,) we have investigated the preparation and properties of a number of inorganic jellies. We have also studied (*J. Phys. Chem.* 1930, **34**, 954) the influence of temperature on the coagulation of various sols and have shown that such sols as hydrous oxides of iron, chromium, tin and aluminium become comparatively unstable when the temperature is raised, whilst easily hydrolysable sols such as prussian blue, gamboge and mastic are stabilised at higher temperatures.

In this communication, we are recording our observations on the influence of temperature on the setting of various jellies. The jelly-forming mixtures were prepared at ordinary temperatures and divided into three portions, and they were allowed to set in thermostats maintained at three different temperatures. The time of setting of the jellies was noted in every case. The setting point of a jelly was sharp enough to take readings with an accuracy of 10 seconds.

The jellies were prepared by methods described in foregoing papers.* Where the jellies were obtained by coagulation, the sols were dialysed for such periods as were necessary to produce jellies of the best texture. So long as the sols were comparatively impure, either no jelles were formed or they gave loose opaque coagulum. In no case the sols could be completely freed from electrolytic impurities, as there was an apprehension of the spontaneous setting of sols to jellies by dialysis alone.

EXPERIMENTAL.

Zirconium Hydroxide Jelly.

*The jelly was prepared by the addition of various quantities of 8.84N-sodium acetate to 3 c. c. of 10% zirconium nitrate

solution, and the volume was made up to 5 c. c. in every case. The mixtures were allowed to set at 30°, 50° and 70°. The results are recorded in the following table.

TABLE I.

0.348N-sodium acetate	Time of setting.		
	30°	50°	70°
0.1 c. c.	No jelly	No jelly	No jelly.
0.2	Do	Do	Do
0.3	Do	Do	Do
0.4	3 hrs.	6 mins.	35 sec.
0.5	2 mins.	30 secs,	Immediately.

The results recorded in this table show that below a certain minimum concentration of sodium acetate, no jelly is formed even at higher temperatures. The time of setting of the jelly is markedly decreased at higher temperatures.

Zirconium Borate Jelly.

The jelly was prepared by dialysing for four days the sol obtained by mixing saturated borax solution with 10% zirconium nitrate solution and coagulating the sol by different amounts of N/5 potassium sulphate.

Concentration of the sol = 24.72 g. zirconium borate per litre.
Amount of sol taken = 3 c. c. Total volume = 5 c. c.

TABLE II.

N/5-K ₂ SO ₄ .	Time of setting.		
	30°	50°	70°
0.4 c. c.	2 hrs.	30 mins.	15 mins.
0.5	16 min.	12	5
0.6	13	11	1
0.7	No jelly but ppt.	4	30 sec.
0.8	No jelly but ppt.	No jelly but ppt.	20 sec. the jelly soon synerises.

Zirconium Molybdate Jelly.

The sol of zirconium molybdate was prepared by mixing 3% potassium molybdate solution with 10% zirconium nitrate solution and dialysing the mixture for 5 days. Concentration of the sol was 14.48 g. zirconium molybdate per litre. The jellies were prepared by coagulating the sol with different amounts of $N/50$ potassium sulphate.

Amount of sol taken = 10 c. c. Total volume = 12 c. c.

TABLE III.

$N/50\text{-K}_2\text{SO}_4$.	Time of setting.		
	30°	50°	70°
1.2 c. c.	No jelly	2 hrs. 30 min.	10 min
1.3	5 hrs.	1 hr. 20 min.	6
1.4	3 hrs. 15 min.	1 hr.	5
1.5	1 hr. 25 min.	29 min	4
1.6	45 min.	22 min	2

Thorium Arsenate Jelly.

This jelly was obtained by mixing different concentrations of 18% potassium arsenate solution with 10 c. c. of thorium nitrate (12.06 g. of the salt per litre), the solution being made up to 12 c.c. in every case.

TABLE IV.

18% KH_2SO_4 .	Time of setting.		
	30°	40°	45°
0.7 c. c.	1 day	No jelly	No jelly
0.8	2 hrs.	Do	Do
0.9	25 min.	Loose jelly in 2½ hrs.	Do
1.0	18	35 min.	2 hrs.
1.1	5	26 min.	90 min.

When the temperature was raised above 50°, the thorium arsenate mixture did not yield any jelly, not even when kept for

five hours. However, if the jelly-forming mixtures be again brought to 30°, they set to jellies.

Thorium Phosphate Jelly.

The jellies of thorium phosphate were prepared by adding varying amounts of 11% potassium phosphate solution to 10 c. c. of thorium nitrate solution (12.06 g. per litre). The total volume was made up to 12 c. c. in every case.

TABLE V.

11% KH_2PO_4 .	Time of setting.		
	30°	40°	45°
0.8 c. c.	No jelly	No jelly	No jelly
0.9	120 min.	66 min.	58 min.
1.0	48	24	20
1.1	16	10	7
1.2	2	2	2

Thorium Molybdate Jelly.

These jellies were prepared by adding varying amounts of 4.5% potassium molybdate to 10 c. c. of thorium nitrate solution containing 12.06 g. of the salt per 250 c. c.

Total volume = 12 c. c.

TABLE VI.

4.5% K_2MoO_4 .	Time of setting.		
	30°	50°	70°
0.9 c. c.	> 60 min.	30 min.	22 min.
1.0	> 60	25	16
1.1	33	20	11
1.2	30	18	10
1.3	28	15	8

Chromium Arsenate Jelly.

The sol was prepared by dialysing the mixture of 100 c. c. of $M/2$ -chromic chloride and 80 c. c. of 18% potassium arsenate

solution for 6 days. It set to jellies when coagulated with $N/5$ potassium sulphate.

TABLE VII.

Concentration of the sol = 36.4 g. per litre.

Amount of sol taken = 10 c. c. Total volume = 15 c. c.

$N/5\text{-K}_2\text{SO}_4$	Time of setting.		
	30°	50°	70°
2.2 c. c.	54 min.	10 min.	1 min.
2.3	36	4	1
2.4	22	3	50 sec.
2.5	15	2	80 sec.
2.6	Ppt.	Ppt.	Ppt.

Vanadium Pentoxide Jelly.

Vanadic acid was precipitated by adding concentrated hydrochloric acid to ammonium vanadate. The precipitate on careful washing passed into a clear red sol, which set to jellies when coagulated with potassium chloride. Concentration of the sol was 1.92 g. vanadium pentoxide per litre.

Amount of sol taken = 5 c. c. Total volume = 12 c.c.

TABLE VIII.

$N/20\text{-KCl}$	Time of setting.		
	30°	50°	70°
1.0 c.c.	3 hrs. 20 min.	No jelly in 8 hrs.	No jelly in 3 hrs.
1.2	38 min.	No jelly in 3 hrs	No jelly
1.3	20	100 min.	Do
1.4	13	45	Do
1.5	4	30	150 min.

Mercuri-sulphosalicylic Acid Jelly.

Mercuri-sulphosalicylic acid was prepared by dissolving 1.5 mols of mercuric oxide in 1 mol. of sulphosalicylic acid and drying the mixture on a water-bath. One gram of the powder thus obtained

was dissolved in 100 c. c. of water. A clear sol with slight opalescence was obtained which set to jellies on addition of $N-K_2SO_4$.

8 c. c. of 1% mercuri-sulphosalicylic acid were taken every time and the total volume was made up to 10 c. c.

TABLE IX.

$N-K_2SO_4$.	Time of setting.		
	30°	40°	50°
0.4	No jelly	No jelly	No jelly
0.5	18 min.	Do	Do
0.6	10	30 min.	Do
0.7	7	15	Do
1.0	1	2	Loose jelly in 8 min.

Zinc Arsenate Jelly.

Zinc arsenate jellies were prepared by taking 5 c. c. of zinc sulphate solution (14.368 g. in 250 c. c.) and adding an equal quantity of water to it and then mixing it with different amounts of 18% potassium arsenate solution. The the total volume was made up to 20 c. c. in every case.

TABLE X.

18% KH_2AsO_4 .	Time of setting.		
	30°	50°	70°
0.16	Did not set	Loose jelly in 60 sec.	Ppt.
0.18	"	90 sec.	80 sec.
0.20	"	60	5
0.30	5 sec.	5	5

Stannic Arsenate Jelly.

To 2 or 3 c.c. of $M/1.099$ -stannic chloride solution were added the varying concentrations of 18% potassium arsenate solution and the total volume was made up to 6 c.c. in every case. A set of the mixture was allowed to set at 20° while the other set was warmed for 5 minutes at 90° and then transferred to ordinary room temperature (20°). The time of gelation was noted in every case.

TABLE XI.

M/1'099-Stannic chloride.	18% Potassium arsenate.	Time of setting.	
		20°	90° (warming)
3'0 c.c.	1 c.c.	23 hrs.	10 hrs.
3'0	2	90 min.	6 min.
3'0	3	25 min.	3
2'0	0'5	24 hrs.	5

• The marked temperature influence observed in the case of this substance is probably due to the fact that warming for a few minutes at a higher temperature causes the hydrolysis of stannic arsenate to stannic oxide. The oxide is also known to yield fine jellies which under the circumstances may set more rapidly than the arsenate jelly.

Stannic Phosphate Jelly.

3 c.c. of M/1'099-stannic chloride solution were mixed with varying amounts of 22 per cent. potassium phosphate solution and the total volume was made up to 6 c.c. in every case. One set of the mixture was allowed to set at 20° while the other at 90°.

TABLE XII.

22% KH_2PO_4 .	Time of setting.	
	20°	90°
0'5 c.c.	22 hrs.	5 min.
1'0	2 hrs.	3
1'5	30 min.	2
2'0	18	1

Stannic Tungstate Jelly.

1'5 or 2 c.c. of 1'53M stannic chloride solution were mixed with different concentrations of 15% sodium tungstate solution. The total volume was made up to 6 c.c. in every case. The mixtures were shaken for five minutes and then transferred to baths at 20° and 98° and the time of gelation was observed.

TABLE XIII.

1.58M-Stannic chloride.	15% Sodium tungstate.	Time of setting	
		20°	98°
2 c.c.	20 c.c.	No jelly	No jelly
2	2.5	No jelly	20 min.
2	3.0	5 days	8
2	3.5	2 days	6
1.5	2.0	>5 hrs.	8

Stannic Molybdate Jelly.

A mixture of stannic chloride in excess and potassium molybdate was dialysed for 24 hours. Concentration of the sol was 91.04 g. SnO_2 per litre. This sol when half diluted gave jellies at different temperatures as follows:

TABLE XIV.

Temp.	...	90°	70°	60°	50°	40°	24°
Time of gelation in min.	...	1	2	4	7	20	360.

Discussion.

The results recorded in the foregoing tables show that in the case of zirconium hydroxide, zirconium molybdate, zirconium borate, thorium molybdate, thorium phosphate, chromium tungstate, stannic arsenate, phosphate, tungstate and molybdate, the time of setting markedly decreases as the temperature is raised.

The jellies of thorium arsenate, vanadium pentoxide and mercuri-sulphosalicylic acid take a longer time to set at higher temperatures, and above a certain temperature, they do not set at all.

No systematic work appears to have been done before on the influence of temperature on the formation of jellies. Fleming (*Z. Phys. Chem.*, 1902, **41**, 427) and Holmes (*J. Phys. Chem.*, 1918, **22**, 516) observed that a slight increase in temperature accelerates the time of setting of silicic acid jelly, while Fells and Firth (*ibid*, 1925, **29**, 248) did not observe any distinct variation with temperature over the range from 0° to 45°. Conflicting results are also found in the case of manganous arsenate jellies (*cf.* Deiss, *Kolloid. Z.*, 1914, **14**, 189; and Kraemer, *Colloid Symp. Monograph*, Wisconsin, 1928, **1**, 66). We have observed that if the manganous chloride and potassium arsenate mixture is warmed at 60° to 80°, it will form manganous

arsenate jelly more conveniently than if the mixture is allowed to remain at ordinary temperature.

Bunce (*J. Phys. Chem.*, 1914, 18, 269) observed that a slight increase in the temperature accelerates the gelation of mercuric oxide jellies but heating for five minutes above 63° seems to prevent the formation of the jelly. Szegvari and Schalek (*Kolloid Z.*, 1923, 32, 318; *ibid.*, 33, 326) observed in the case of iron oxide jelly that the setting time decreases with the rise in temperature.

In the case of organic jellies, like gelatin, agar agar, soap, starch, pectin and others, the behaviour is quite different. The lowering of temperature always favours their gelation. These jellies also undergo a sort of melting when temperature is raised and the melted sol again assumes the jelly form when cooled, and thus, these jellies are heat reversible. Most of the inorganic jellies do not show this sort of reversibility.

The change in temperature in case of jelly-forming mixtures causes the variation in the solubility of the dispersed phase, in the degree of hydrolysis, in the hydration of particles and in the rate of coagulation. The setting time appears to be a complicated function of all these factors. Organic substances, due to the marked temperature influence on the solubility, form both true and colloidal solutions, and at different temperatures an equilibrium exists between the molecules and colloidal aggregates. As the temperature is lowered, due to the decrease in solubility, the colloidal phase begins to preponderate, which on developing surficial and structural hydration under suitable conditions, sets to a jelly.

With the exception of those inorganic sols which appear to undergo marked hydrolysis with rise in temperature, the rate of coagulation is markedly increased if the temperature is raised and with the rapid decrease in charge, the viscosity and hydration of particles also increase. Thus a jelly is obtained in a comparatively shorter time at higher temperatures. The sols undergoing hydrolysis at higher temperatures become stable towards coagulation and as such, the jelly takes more time to set. The agglomeration tendency of the particles also appears to be favoured at higher temperatures and consequently, the jellies obtained at higher temperatures are more opalescent.

In the case of polybasic salts of heavy metals, like tin, zirconium, thorium and others, it is highly probable that as the temperature increases, they are hydrolysed and hydrous oxides are formed. In

case of such substances, the hydrous oxides also have a tendency of developing hydration, and some times greater than the corresponding polybasic salts. In such cases of mixed jellies, the time of setting would depend upon the hydration developed by different phases.

The jelly of mercuri-sulphosalicylic acid resembles more or less the organic jellies, whose setting is favoured by the lowering of temperature. It appears that the anomalous thorium arsenate and vanadium pentoxide jellies exhibit when freshly formed what is known as the 'melting of jellies,' a phenomenon so common in the case of organic jellies. It has been found that though a jelly-forming mixture of thorium arsenate remains liquified at 60° , the jelly of the same concentration prepared at ordinary temperature, but allowed to age for some hours does not undergo melting if the temperature is raised. A similar observation has been made in the case of vanadium pentoxide. This appears to be partly due to the decrease in the hydration tendency and partly to the decrease in the surface energy on ageing. This effect is not so marked in the case of organic jellies which are, consequently heat reversible.

Summary.

1. The influence of temperature on the setting of various inorganic jellies has been investigated. It has been observed that all the inorganic jellies with the exception of thorium arsenate, vanadium pentoxide and mercuri-sulphosalicylic acid, set more readily at higher temperatures than at low. The jellies (these three exceptions) are not formed above 60° .

2. In the case of such inorganic sols which do not undergo hydrolysis, the rise in temperature increases the rate of coagulation, and consequently, the hydration is more rapidly developed and the jellies are readily obtained.

3. The jellies of polybasic salts are hydrolysed at higher temperatures to the corresponding hydroxides which have also a tendency to form jellies, and hence the setting time would depend upon the tendency of mixed phases.

4. The jellies of vanadium pentoxide and thorium arsenate show the 'melting phenomenon' at higher temperatures.

In conclusion, the author wishes to express his indebtedness to Prof. N. R. Dhar for his very kind interest and guidance in this work.

A New Method of Estimating Arsenic in Organo-arsenic Derivatives. Part II.

BY HIRENDRA NATH DAS-GUPTA.

The present communication is a continuation of the work done by the author (*J. Indian Chem. Soc.*, 1932, 9, 95), on the problem of estimating arsenic accurately and rapidly in organo-arsenic compounds. There was, however, the limitation that the compounds concerned should contain arsenic in the penta-valent state. The present paper deals with those derivatives in which the metalloid is in the tri-valent state.

Organo-arsenic compounds containing tri-valent arsenic do not liberate iodine from potassium iodide in hydrochloric acid solution and hence the previous method (*loc. cit.*) could not be followed. A careful study of the properties of organo-arsenic derivatives, in which the element is present in the tri-valent state, clearly reveals the fact that most of the compounds are unstable and readily undergo oxidation either simply by atmospheric influence or when treated with simple oxidising agents and are thus converted into corresponding arsinic acids. Advantage was taken of this particular phenomenon, as the acid thus produced readily liberates an equivalent amount of iodine from potassium iodide in hydrochloric acid solution. Hydrogen peroxide was used throughout the experiments as the common oxidising agent. In some cases simple treatment with hydrogen peroxide in the cold was sufficient to bring about the complete oxidation of the compound, whilst in others the peroxide mixture required to be heated for the attainment of the desired result. It was found rather difficult to destroy the excess of the peroxide left after the reaction, by heating either on water-bath or by direct flame and hence to obviate this difficulty, the hot solution, previous to its treatment with acid mixture, was treated with potassium iodide whereby the excess of the peroxide liberated the equivalent amount of iodine. The iodine thus liberated was subsequently treated with $N/10$ -sodium thiosulphate solution till the last trace of iodine was removed. This treatment does not interfere with the subsequent steps as the metalloid in the penta-valent state liberates iodine only in acid solution.

After the complete oxidation of the product the same procedure was followed as described in part I (*loc. cit.*).

Compounds selected for analyses belong to different types containing different groupings in the nucleus. The compounds of the arsa-zine series in which arsenic is in the ring *e.g.*, phenarsazine chloride (Burton and Gibson, *J. Chem. Soc.*, 1926, pp. 451, 467, 469) ; phenarsazine acetate (Burton and Gibson, *J. Chem. Soc.*, 1924, 125, 2277) ; phenarsazine oxide (Burton and Gibson, *J. Chem. Soc.*, 1926, p. 462) and phenarsazine methyl ether, have been analysed and found to give good results. The method is very simple and requires only a small quantity of the substance (10-20 mg.) for analysis. The method of arsenic estimation devised by Norton and Koch (*J. Amer. Chem. Soc.*, 1905, 27, 1247) failed in the cases of quinoline compounds containing arsenic, but no such difficulty was encountered by adopting this method.

The following table summarises the experimental results of the present investigation.

EXPERIMENTAL.

Substance.	Quantity taken.	$\text{Na}_2\text{S}_2\text{O}_3$ 1·002-N/20.	Arsenic content Found.	Calc.
Phenylarsenious chloride	0·0140 g. 0·0168	5 c.c. 6	33·55 33·54	33·6 p.c.
Phenylarsenious oxide	0·0201 0·0196	9·55 9·35	44·63 44·56	44·6
Arsenobenzene	0·0213 0·0154 0·0213 0·0254	11·20 8·10 11·20 13·35	49·29 49·30 49·29 49·30	49·8
Neosalvarsan	0·0278 0·0242	9·55 8·30	32·20 32·20	32·1
10-Chloro-5 :10-dihydrophenarsazine	0·0171 0·0213	4·90 6·10	26·91 26·90	27·02
10 :10'-Oxy-5 :10-dihydrophenarsazine	0·0137 0·0145	4·40 4·65	30·10 30·10	30·00
Phenarsazine-methyl ether.	0·0158 0·0162	4·60 4·70	27·35 27·31	27·47
10-Chloro-5-acetyl-5 :10-dihydrophenarsazine	0·0192 0·0224	4·80 5·60	23·4 23·4	23·47

Procedure.—The finely powdered substance (10-20 mg.) was taken i

a 300 c.c. conical flask and was covered with 10 c.c. of hydrogen peroxide (12 vol.). The mixture was heated on a water-bath for 15 minutes in order to effect complete oxidation of the substance as seen by its gradual dissolution in excess of the peroxide with change in coloration. In case heating on water-bath did not bring about complete oxidation, the flask was heated over an asbestos board by a low flame after supporting a funnel on the mouth of the flask. The funnel was subsequently washed with distilled water and the washings allowed to run into the main bulk. The oxidised solution was next cooled to the room temperature and then treated with excess of potassium iodide. The unreacted peroxide present at once liberated the equivalent amount of iodine with rise in temperature and the solution assumed a deep brown coloration. The iodine thus set free was gradually treated with *N*/10-sodium thiosulphate solution. Towards the end 2 c.c. of 1 per cent. solution of starch were added and the addition of thiosulphate solution continued till the blue coloration due to free iodine with starch faded away. Owing to the fact that solution of certain organic derivatives are coloured brown, one is apt to be misled by not being able to ascertain whether the existing brown colour is due to free iodine or due to the compound itself; it is therefore advisable to add the starch solution at an earlier stage. (In case the tri-valent derivative under analysis contain a halogen linked to arsenic, the following additional treatment is necessary as the oxidation of such chloro compound gives the corresponding amount of hydrochloric acid. To the oxidised product 2 drops of methyl orange added and then treated drop by drop with *N*/10-sodium carbonate solution till the pink colour changed to yellow. After this the addition of potassium iodide was made as given above). The walls of the flask were then washed carefully with water and the solution cooled. To this glacial acetic acid (15 c.c.) and hydrochloric acid (*d* 1.19, 15 c.c.) were added. The solution immediately assumed a blue coloration due to the liberation of iodine from excess of potassium iodide by the metalloid in acid medium with rise in temperature. The solution was therefore, cooled at first and 2 g. more of potassium iodide were added and the liberated iodine was titrated against *N*/20-sodium thiosulphate. As before, the point at which the blue colour just disappears is not the true end point and the addition of the thiosulphate solution should be continued till there is no change in coloration. This is best ascertained by allowing a drop of the standard thiosulphate solution to fall on the solution

and observing whether there is any change in the region in which the drop is allowed to fall. From the amount of the sodium thiosulphate solution required the percentage of the arsenic is calculated from the following relation :

1 C.c. of *N*/20-thiosulphate \equiv 0.0009375 g. of arsenic.

Summary.

Uptil now there is no satisfactory qualitative test for ascertaining the presence of arsenic in a new compound obtained by an attempt to introduce arsenic into the same. The method given may be used as a qualitative test for determining the presence of arsenic.

Nitroarsinic acid derivatives on being reduced by the usual reducing agents might give either an aminoarsinic acid derivative or a nitroarseno derivative. In such doubtful cases the above test is very suitable as the liberation of iodine in acid solution takes place only with the penta-valent derivatives.

Arsenic in quinoline compounds is best determined by this method.

In conclusion the author takes the pleasure in expressing his grateful thanks to Dr. M. Goswami for his keen interest in the present investigation and for placing all the resources of his laboratory at his disposal and to the Director of Public Instruction, Bengal, for awarding him a Post-Graduate Research Scholarship which has enabled him to undertake the work.

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Studies in Quinoline Compounds. Part VII.

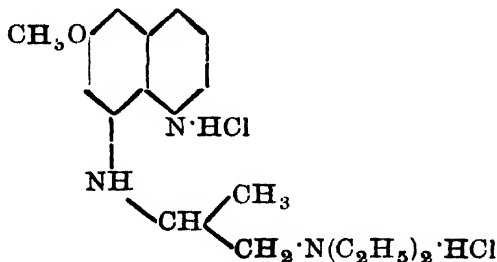
BY UPENDRANATH BRAHMACHARI AND JNANENDRA
MOHAN DAS-GUPTA.

In part VI of the series of papers (*J. Indian Chem. Soc.*, 1932, 9, 37) we described the preparation of 6-methoxy-8-aminoisopropylaminoquinoline dihydrochloride which is structurally related to plasmoquine. It occurred to us that by ethylation we could enhance the similarity of this compound with plasmoquine and expected that they might possess some antimalarial properties. Other simpler aminoquinoline derivatives have also been synthesised with the same end in view.

Attempts to prepare the alkylated products by condensing β -bromopropylalkylamines with aminoquinolines were unsuccessful.

EXPERIMENTAL.

6-Methoxy-8- β -diethylaminoisopropylaminoquinoline Dihydrochloride.



6-Methoxy-8- β -aminoisopropylaminoquinoline dihydrochloride (3.1 g.) (*loc. cit.*) was dissolved in water (15-20 c.c.) and treated with anhydrous sodium carbonate (4 g.) when the corresponding base was precipitated as a viscous sticky mass. After the addition of a little more than the theoretical quantity of ethyl iodide the mixture was refluxed for 2½ hours on a water-bath. The alkylated product floated as an oil and was extracted with ether. The ethereal solution was dried over anhydrous potassium carbonate and a dry current of hydrochloric acid gas passed through it when the dihydrochloride was

precipitated but soon coalesced. The precipitate was next dissolved in a little absolute alcohol from which it crystallised out as a solid yellow crystalline substance readily dissolving in water to a clear yellow solution, m.p. 175° . (Found: N, 11.75; Cl, 19.53. $C_{17}H_{27}ON_3Cl_2$ requires N, 11.66, Cl, 19.72 per cent.).

6-Methoxy-8-β-dimethylaminoisopropylaminoquinoline dihydrochloride.—6-Methoxy-8-β-aminoisopropylaminoquinoline dihydrochloride (4.5 g.) dissolved in water (12 c.c.) was refluxed on a water-bath with N_2CO_3 (6 g.) and CH_3I (5.2 g.) for 2-3 hours. The dihydrochloride was prepared as before. It is a yellowish brown crystalline compound easily dissolving in water, m.p. 180° . (Found: N, 12.70; Cl, 21.33. $C_{15}H_{23}ON_3Cl_2$ requires N, 12.65; Cl, 21.38 per cent.).

8-β-Dimethylaminoisopropylaminoquinoline dihydrochloride was prepared from 8-β-aminoisopropylaminoquinoline dihydrochloride (*loc. cit.*). It is a yellowish brown powder, m.p. $200-205^{\circ}$. (Found: N, 14.04; Cl, 23.40. $C_{14}H_{21}N_3Cl_2$ requires N, 13.90; Cl, 23.51 per cent.).

6-Methyl-8-β-dimethylaminoisopropylaminoquinoline dihydrochloride was also prepared from 6-methyl-8-aminoisopropylaminoquinoline hydrochloride, m.p. 210° . (Found: N, 13.22; Cl, 22.32. $C_{15}H_{23}N_3Cl_2$ requires N, 13.29; Cl, 22.46 per cent.).

2-Methyl-6-methoxy-8-β-dimethylaminoisopropylaminoquinoline dihydrochloride prepared from 2-methyl-6-methoxy-8-aminoisopropylaminoquinoline dihydrochloride in the usual way, melts at 218° . (Found: N, 12.00; Cl, 20.33. $C_{16}H_{25}ON_3Cl_2$ requires N, 12.14; Cl, 20.52 per cent.).

β-Hydroxypropyl-8-aminoquinoline hydrochloride.—Allyl-8-aminoquinoline hydrochloride (1 g.) (*loc. cit.*) was warmed with fuming HBr (5 c.c.) on a water-bath for 15-30 minutes. Excess of HBr was partly removed on the water-bath in a basin and the cooled mixture was next made alkaline. β-Bromopropyl-8-aminoquinoline was precipitated as an oil and was extracted with ether. The ethereal solution was dried and the ether removed when an oily substance was obtained which solidified on cooling and scratching and purified from alcohol.

A mixture of β-bromopropyl-8-aminoquinoline (1.2 g.) and water (10-12 c.c.) was gently boiled with Na_2CO_3 (2 g.) for 8-4 hours and the oil that separated was extracted with ether. The hydrochloride was prepared as usual and crystallised from alcohol. It melts at $170-72^{\circ}$.

That it is the β -hydroxy derivative follows from the fact that it can as well be prepared by condensing chloroisopropyl alcohol with 8-aminoquinoline in the usual way. It is thus proved that it is the β -bromo- and β -hydroxy-compounds that are formed in the former method. (Found: N, 11.80; Cl, 15.00. $C_{12}H_{15}ON_2Cl$ requires N, 11.74, Cl, 14.88 per cent.).

6-Ethoxy- β -hydroxypropyl-8-aminoquinoline hydrochloride.—6-Ethoxy-8-*n*-allylaminoquinoline hydrochloride (0.5 g.) was treated with fuming HBr (5 c.c.) and was then proceeded with as above. The hydrochloride melts at 165° and is hydrolysed by water. (Found: N, 10.02; Cl, 12.32. $C_{14}H_{19}O_2N_2Cl$ requires N, 9.91; Cl, 12.56 per cent.).

8-n-Lactylaminoquinoline hydrochloride.—8-Aminoquinoline (0.5 g.) and ethyl lactate (0.8 g.) were heated together in an oil-bath at 130° for 2½ hours. The mixture was cooled, treated with dilute hydrochloric acid and shaken with ether to remove oily insoluble matters. The aqueous solution was filtered, made alkaline and extracted with ether from which the hydrochloride was precipitated by passing dry HCl gas. It was further purified by crystallisation from alcohol. It is a light yellow crystalline powder which is hydrolysed by water, m. p. 182-85°. It also results from heating the lactate of 8-aminoquinoline at 175° for 2 hours. (Found: N, 11.21; Cl, 14.22. $C_{12}H_{13}O_2N_2Cl$ requires N, 11.09; Cl, 14.06 per cent.).

8-*n*-Lactylamino-6-ethoxyquinoline hydrochloride was obtained similarly from ethyl lactate and 6-ethoxy-8-aminoquinoline. The hydrochloride which hydrolyses with water melts at 177°. (Found: N, 14.02; Cl, 18.21. $C_{14}H_{17}O_3N_2Cl$ requires N, 14.25; Cl, 18.06 per cent.).

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Dyes Derived from Phenanthraquinone : Fluorenophenanthrazines.

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CHANDRA DE.

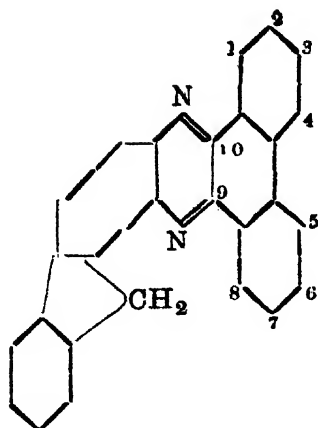
In continuation of the work of Watson and Dutt on phenanthraphenazines (*J. Chem. Soc.*, 1921, 119, 1211) and Sircar and Dutt on phenanthranaphthazines (*J. Chem. Soc.*, 1922, 121, 1944), the present investigation was undertaken with a view to study if the complexity of the ring has any deepening effect on the colour of the monoazine dyes. The present communication deals with azine dyes obtained by condensing phenanthraquinone and its derivatives with 1:2-diaminofluorene (Diels, Schill and Tolson, *Ber.*, 1902, 35, 3284). The compounds prepared are all deeper in shade than those of the corresponding phenanthraphenazines and the phenanthranaphthazines.* For the sake of convenience a comparison of the colours of dyeings of wool of some of these classes of compounds is given in Table I.

TABLE I.

Name of the compound.		Colour of the dyeing wool.
4-Nitrophenanthranaphthazine	...	Light yellow
Fluoreno-4-nitrophenanthrazine	...	Deep brown
4:5-Dinitrophenanthranaphthazine	...	Yellow
Fluoreno-4:5-dinitrophenanthrazine	...	Chocolate
2-Aminophenanthraphenazine	...	Yellow
Fluoreno-2-aminophenanthrazine	...	Chocolate brown
2-Hydroxyphenanthranaphthazine	...	Yellow
Fluoreno-2-hydroxyphenanthrazine	...	Chocolate

The compounds dissolve in concentrated sulphuric acid with a deep blue colour and the original dyes are reprecipitated by the addition of water and in this condition they are well suited for dyeing on wool from an acid bath. They are characterised by their high melting points and their sparing solubility in alcohol and acetic acid.

The structure of these compounds can be represented by the following general formula.



For the sake of abbreviation the preparation of only one of these compounds is described and the rest, except the 2-amino- and the 4-amino-compounds where in place of acetic acid absolute alcohol was taken, being prepared in similar manners, their properties recorded in Table II.

EXPERIMENTAL.

Fluorenophenanthrazine.—Molecular quantities of phenanthraquinone and 1:2-diaminofluorene in acetic acid solutions were mixed together and boiled for 1 hour when the substance separated out as a greenish-brown crystalline precipitate which was filtered, washed with acetic acid and alcohol and recrystallised from nitrobenzene in thin brown needles, m. p. 279-80°. It is insoluble in alcohol, sparingly soluble in acetic acid and moderately soluble in pyridine. It dissolves in concentrated sulphuric acid with a blue colour and dyes wool in yellow shade.

TABLE II.
Dyes Derived from Phenanthraquinone.
P = Phenanthrazine, P = Phenanthraquinone).

Name.	Prepared from 1:2-diaminofluorene and	(F = Fluoreno; P = Phenanthrazine, P = Phenanthraquinone).	Appearance.	Crystallised from	Shade on wool.	Found.	Analysis.	Calc.
F-P *	P		Thin brown needles.	Nitrobenzene	Yellow	N, 7.40		7.60 p.c.
F-2-nitro-P	2-Nitro-P		Chocolate needles.	"Pyridine	Chocolate brown	N, 10.04		10.16
F-4-nitro-P	4-Nitro-P		Greenish-brown crystalline mass.	"	Deep "	N 10.08		10.16
F-2:7-dinitro-P	2:7-Dinitro-P		Yellow prismatic needles.	Nitrobenzene	Yellow	N, 12.13		12.22
F-4:5-dinitro-P	4:5-Dinitro-P		Chocolate brown small needles.	Pyridine	Chocolate	N, 12.15		12.22
F-2-bromo-P [†]	2-Bromo-P		Brown crystalline mass.	Acetic acid	Brown	N, 6.10		6.26
F-2-amino-P	2-Amino-P		Brown microscopic needles.	Pyridine	Chocolate brown	N, 11.01		10.96
F-4-amino-P	4-Amino-P		"	"	Deep "	N, 10.83		10.96
F-2:7-diamino-P	2:7-Diamino-P		"	"	Yellowish "	N, 14.00		14.07
F-2-hydroxy-P	2-Hydroxy-P		Chocolate brown needles.	Acetic acid	Chocolate	N, 7.21		7.29
F-4-hydroxy-P	4-Hydroxy-P		Brown crystalline mass.	"	Greenish brown	N, 7.18		7.29
F-2:1-dihydroxy-P	2:7-Dihydroxy-P		Chocolate brown crystalline mass.	"	" "	N, 6.81		7.00

* Fluorenophenanthrazine melts at 279-80°. The rest melts above 290°.

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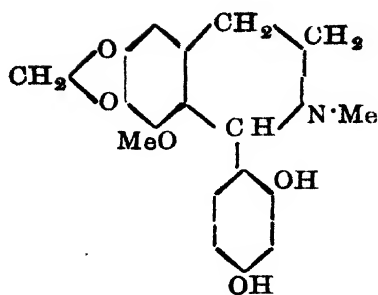
Studies in Chemotherapy. Part III. (Attempts to Prepare Antimalarials). Derivatives of Cotarnine.

BY GURCHARAN SINGH AHLUWALIA, BASHESHAH DAS KOCHHAR
AND J. NANENDRA NATH RAY.

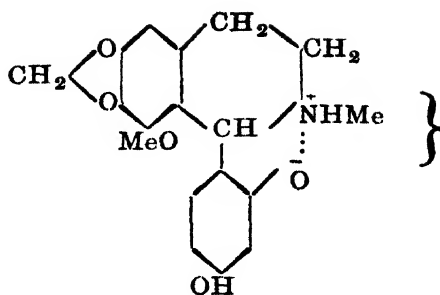
• In the report of Opium Commission of 1893 (Government of India) it is stated that opium may have an antimalarial action. Narcotine is stated to resemble quinine in its tonic and anti-periodic properties. Gordon (*Indian Annals of Medical Science*, Vol. VII) confirmed the prophylactic value of narcotine. But recently Chopra and Knowles (*Ind. J. Med. Res.*, 1930, 18, 5) have arrived at the conclusion that narcotine has no curative or prophylactic value in malaria, even in large doses. At the suggestion of Central Board of Revenue (Government of India) the present investigation of converting narcotine into a febrifuge, preferably an antimalarial, was undertaken.

Cotarnine has now been condensed with phenols, e.g., phloroglucinol, resorcinol and pyrogallol, the reaction proceeding with diminishing ease in the order given. It has been established (Ahluwalia, Narang and Ray, *J. Chem. Soc.*, 1931, p. 2057) that in these condensations probably the nuclear hydrogen atom of the phenol molecule takes part. Anhydrocotarnine-resorcinol (I) or (IA) * has now been found to have antipyretic action favourably comparable to quinine and its toxic action to *paramoecium* (cf. its structure with hexyl resorcinol) is greater in equivalent dilution than quinine. The details of these experiments will be published elsewhere. Cotarnine also condenses with 1-phenyl-3-methylpyrazolone, 3-methylpyrazolone, 3:5-dimethylpyrazole, 3-methyl-5-phenylpyrazole, 1:5-diphenyl-3-methylpyrazole to give corresponding anhydrocotarninopyrazoles. In the formation of these substances (III) probably a carbon to carbon linkage is established since 1:5-diphenyl-3-methylpyrazole (II) can only react if such is the case.

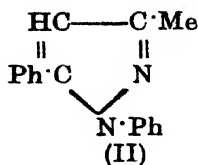
* Certain results obtained since the paper was written up indicate that the substance may also be (IA).



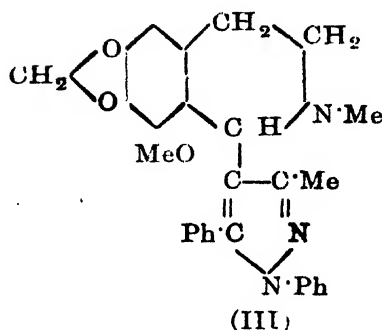
(I)



(IA)



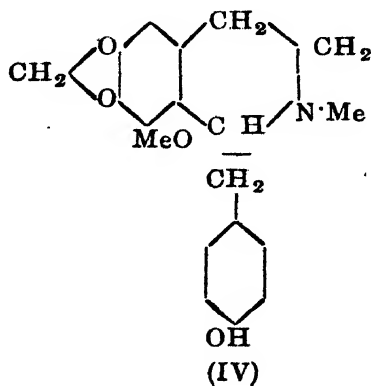
(II)



(III)

Foulds and Robinson (*J. Chem. Soc.*, 1914, 105, 1970) also assume that in the condensation of cotarnine with α -methylindole, neither the imino group nor the methyl group was involved but the condensation took place at the β -carbon atom of the indole nucleus.

Hope and Robinson's *anhydrocotarnino-p-nitrotoluene* (*J. Chem. Soc.*, 1911, 99, 2114) has now been reduced to the corresponding amino compound and from it a new alkaloid (IV), which may be regarded as belonging to laudanidine group has been prepared.



(IV)

Certain of the above compounds have been tested in respect of their antimalarial action. The numbers given in parentheses in the experimental portion, are to facilitate reference to biological tests. The antipyretic properties of the compounds described in the paper has been investigated. The results are given at the end of the paper. The antimalarial properties are being studied.

EXPERIMENTAL.

Oxidation of Narcotine to Cotarnine.

•The following process worked better than the method given by Rakshit (*J. Chem. Soc.*, 1918, 113, 469).

Nitric acid (*d* 1.4,66 g.) in water (160 c.c.) was heated till the temperature was 49°. To this finely powdered narcotine (20 g.) in small portions was added with vigorous shaking, the whole operation lasting 1½ hours, the temperature being maintained at 49° all the time. The felt-jacketed reaction vessel, which may also be a thermo-flask, was set aside for 12 hours, and then the solution filtered from the oily deposit. The strongly cooled filtrate was basified with concentrated sodium hydroxide solution, the precipitated cotarnine collected, washed with ice-water, dried and crystallised from benzene, m.p. 132°, yield 10.5 g. The mother liquor furnished opianic acid on acidification.

Anhydrocotarnino-resorcinol (I): 1-(2':4'-Dihydroxyphenyl) hydrocotarnine (R 76).

A mixture of resorcinol (2.2 g.), cotarnine (4.7 g.) and alcohol (*absolute*, 52 c.c.) was warmed on the steam bath at 40-45° for 15 minutes. The pale yellow crystalline deposit well washed with alcohol, was collected after standing some time, yield 6 g. (*cf.* Liebermann, *Ber.*, 1904, 37, 2744). The substance does not dissolve in benzene and ether but dissolves readily in dilute acid and alkali solutions without hydrolysis. (Found: N, 4.8. $C_{18}H_{19}O_5N$ requires N, 4.8 per cent.).

The substance (2 g.) was mixed with *N/2-HCl* solution (12.2 c.c.) and the clear solution cooled when the *hydrochloride* (R 77) crystallised out in short prisms, m.p. 240°. (Found: N, 4.1. $C_{18}H_{19}O_5N$. *HCl* requires N, 3.8 per cent.).

The substance in 1:15,000 dilution completely arrests the movement of *paramoecium* and kills 20 per cent. in 54 hours

whilst quinine is without effect at the same concentration on the same strain of *paramoecium*. The substance decreases the tone and amplitude of the contractions of muscles and produces an immediate contraction in isolated uterus and thus differs from cotarnine which causes slow tonic contraction. The uterus does not relax after washing with Ringer's solution, as is the case with adrenaline; thus it resembles quinine hydrochloride. The substance has no effect on the shape of contraction of striped muscle. In a dilution of 1:10,000 to 1:50,000 it causes diastolic dilatation with decreased amplitude of contraction of the cardiac muscle; the frequency is also decreased which is followed later on by impaired conduction of impulses resulting in partial or complete heart block. However, the vagus endings are not involved in the effect of the drug on heart, therefore, it directly acts on the cardiac muscles.

1-(2:3:4 *Trihydroxyphenyl*) *hydrocotarnine* (R 91) similarly prepared from pyrogallol (2.5 g.) and cotarnine (4.7 g.) in alcohol (15 c.c.) had m.p. 211°. (Found N, 4.2. $C_{18}H_{19}O_6N$ requires N, 4.1 per cent.).

1-(2:4:6- *Trihydroxyphenyl*) *hydrocotarnine* (R 87), m.p. 170° and the *hydrochloride*, m.p. 185° (decomp.) were similarly prepared. (Found: N, 3.4. $C_{18}H_{19}O_6N$, HCl requires N, 3.7 per cent.).

Anhydrocotarnino-1-phenyl-3-methylpyrazolone (R 88) (formula analogous to III).—A mixture of 1-phenyl-3-methylpyrazolone (3.5 g.) in absolute alcohol (20 c.c. containing sodium ethylate from 0.2 g. of sodium) and cotarnine (4.7 g.) was heated on the steam-bath till a clear solution resulted, then on standing a colourless crystalline material deposited, m.p. 177°, yield 6.7 g. (R 73).

The substance is insoluble in benzene, acetone and chloroform but is soluble in hot alcohol and with decomposition in hot water. At 155°, the substance becomes brownish yellow. (Found: N, 10.5. $C_{22}H_{23}O_4N_3$ requires N, 10.7 per cent.).

Similarly, when a solution of 3-methylpyrazolone (2.0 g.) in hot alcohol (10 c.c.) was added to a hot solution of cotarnine (4.7 g.) in alcohol (15 c.c.), the corresponding anhydrocotarninopyrazolone, m.p. 199° (decomp.) crystallised out on standing. The substance is phototropic. It dissolves to a colourless solution in hydrochloric acid without apparent decomposition. (Found: N, 13.5. $C_{16}H_{19}O_4N_3$ requires N, 13.8 per cent.).

3:5-*Dimethylpyrazole* (3 g.), prepared from acetylacetone and hydrazine hydrate, when interacted with a hot solution of cotarnine (4 g.) in alcohol furnished *anhydrocotarnino-3:5-dimethylpyrazole*

after standing 4 hours, m.p. 140° after recrystallisation from hot alcohol. (Found: N, 13.6. $C_{17}H_{21}O_3N_3$ requires N, 13.8 per cent.). *Anhydrocotarnino-3-methyl-5-phenylpyrazole*, m. p. 146° after changing colour at 1.7° (R 95) was similarly prepared from the corresponding pyrazole. (Found: N, 11.4. $C_{22}H_{23}O_3N_3$ requires N, 11.2 per cent.).

Anhydrocotarnino-1:5-diphenyl-3-methylpyrazole (R 98) was deposited from a warm solution of cotarnine (5 g.) and 1:5-diphenyl-3-methylpyrazole (5 g.) in absolute alcohol (15 c.c.) after standing for 1 hour and had m. p. 148° after crystallisation from alcohol. (Found: N, 9.6. $C_{28}H_{27}O_3N_3$ requires N, 9.3 per cent.).

Anhydrocotarnino-p-nitrotoluene can be obtained in a good yield by the following modification of Hope and Robinson's process (*loc. cit.*). Cotarnine (10 g.), and *p*-nitrotoluene (15 g.) in dry alcohol (100 c.c. containing sodium ethylate from 1 g. of sodium) was warmed at $40-45^{\circ}$ for 15-20 minutes. The product obtained after standing 12 hours had m.p. 121° , yield 8 g. No difficulty was experienced in reducing the substance (*cf.* however, Gulland and Virden, *J. Chem. Soc.*, 1929, p. 1793). The nitro compound (9 g.) was gradually added to a mixture of stannous chloride (18 g.) hydrochloric acid (*d* 1.16, 36 c.c.) water (30 c.c.) and was shaken for 20 hours at $28-32^{\circ}$. The clear filtrate obtained after dilution with water furnished the amino compound when strongly basified with sodium hydroxide solution. The substance separates as pale yellow needles, m. p. 95° from hot dilute alcohol, yield 6.8 g. (Found: N, 8.6. $C_{19}H_{22}O_3N_2$ requires N, 8.6 per cent.).

Anhydrocotarnino-p-hydroxytoluene (IV, R 90).—A solution of anhydrocotarnino-*p*-aminotoluene (3.5 g.) in sulphuric acid (20 c.c. of 10 p. c.) was diazotised with a solution of sodium nitrite (0.7 g.) in water (3 c.c.) at 0° . The mixture was allowed to stand at room temperature for a few days, then made alkaline with sodium carbonate, and the precipitated phenol thrice crystallised from hot dilute alcohol (charcoal), m. p. 191° . (Found: N, 4.5. $C_{19}H_{21}O_4N$ requires N, 4.3 per cent.).

Anhydrocotarnino-p-phenetidine (R 96) was obtained from cotarnine (4.7 g.), phenetidine (2.7 g.), alcohol (15 c.c.) and sodium (0.1 g.) by gentle warming for $\frac{1}{2}$ hour and then standing for 3-4 hours. The yield is much poorer without sodium ethylate. Recrystallised from a mixture of benzene and ligroin it melts at 126° , yield 4.2 g. (Found: N, 7.9. $C_{20}H_{24}O_4N_2$ requires N, 7.9 per cent.).

The *hydrochloride*, m. p. 239° (after crystallisation from methanol) was obtained from the benzene solution of the base by hydrogen chloride at 0° . Similarly *anhydrocotarnino-o-phenetidine* (R 97) m. p. 126° was prepared from *o*-phenetidine in a 85 p. c. yield, care being taken not to prolong the heating beyond $\frac{1}{2}$ hour. (Found: N, 8.1. Calc. N, 7.9 per cent.).

Anhydrocotarnino-p-anisidide, m. p. 124° (Found: N, 8.3. $C_{19}H_{22}O_4N_2$ requires N, 8.2 per cent.) and the *o-anisidide*, m. p. 134° (Found: N, 8.3 per cent.) were prepared from *p*- and *o*-anisidine respectively.

Pharmacological.

[WITH DR. KHEM SINGH GRAVAL, M.B., B.S., PH.D.]

TABLE I.

Effect of Different Dilutions of the 2':4'-Dihydroxyphenylcotarnine Hydrochloride and Quinine on *Paramoecium* in 24 hours.

Dilution.	2' :4'.Dihydroxyphenyl- hydrocotarnine hydrochloride.	Quinine hydrochloride
1 :40,000	All dead	All dead
1 :50,000	do	do
1 :75,000	do	do
1 :100,000	do	do
1 :150,000	20% dead	All alive
1 :200,000	All alive	do

TABLE II

Effect of 2':4'-Dihydroxyphenylcotarnine Hydrochloride and Quinine Hydrochloride in higher Concentrations on *Paramoecium*.

Concentration of the drug used.	Movements become sluggish. Time in minutes.		Death Time in minutes	
	2' :4'-Dihydroxy- phenylcotarnine hydrochloride (R 77).	Quinine hydrochloride.	2' :4'-Dihydroxy- phenylcotarnine hydrochloride.	Quinine hydrochloride
1 :500	At once	At once	At once	At once
1 :1000	do	0.33	1.3	0.6
1 :2000	0.5	1.0	2-2.5	1.3
1 :3000	1.0	1.5	4.0	2.0
1 :4000	2.0	3.0	5.6	3.5
1 :8000	5.0	6.0	22.0	10.0
1 :16000	6.7	15.0	50.0	28-33

TABLE III.

Daily Record of the Rectal Temperature of Rabbits in F°.

Rabbits marked.	Date.	8 A.M.	11 A.M.	2 P.M.	5 P.M.
A	March 6th 1931	102.1	102.2	102.0	—
	7th 1931	102.4	101.7	102.2	103.2
	8th 1931	101.8	101.4	102.8	102.4
	9th 1931	102.0	102.1	102.8	103.0
B	6th 1931	102.2	102.2	102.2	—
	7th 1931	102.0	101.4	101.9	102.3
	8th 1931	101.9	101.4	102.0	101.4
	9th 1931	101.2	101.7	101.0	102.2
C	6th 1931	102.0	101.8	102.0	—
	7th 1931	102.0	101.1	101.6	101.6
	8th 1931	101.3	101.4	102.7	102.2
	9th 1931	101.8	102.8	101.6	102.8
D	6th 1931	101.7	102.3	102.5	—
	7th 1931	102.7	102.1	102.3	102.7
	8th 1931	102.4	101.9	102.8	102.7
	9th 1931	102.0	102.9	102.6	103.0
E.	6th 1931	102.0	101.3	101.4	—
	7th 1931	101.4	101.1	101.4	101.1
	8th 1931	101.8	101.2	101.4	101.6
	9th 1931	101.5	101.2	101.0	101.6

TABLE IV.

Change in temperature after injecting 4.5 c.c. of bacillus *coli. communis* emulsion subcutaneously in the left thigh at 9.30 A.M. and the drugs (100 mg.) injected subcutaneously in the right thigh at 2 P.M. Temperature is shown in F° and the weight in kilos.

Time.	A.	B.	C.	D.	E.
Weight	1.64	1.45	1.7	1.1	1.5
9.30 A.M.	102.2	102.2	102.5	102.6	101.6
10.30	102.4	102.6	102.5	102.9	101.6
11.00	102.6	103.8	103.2	103.2	101.8
11.30	103.8	105.0	103.7	104.6	103.0
12.00	104.6	105.2	104.5	104.8	104.0
12.30 P.M.	104.7	106.0	105.8	105.0	104.4
1.00	104.8	106.0	105.6	105.4	105.0
2.00	104.8	106.0	105.6	105.5	105.0

TABLE IV—(contd.).

	Aspirine.	Quinine hydrochloride.	2':4' Di-hydroxyphenylcotarnine hydrochloride.	Cotarnine hydrochloride.	p-Ethoxyaminophenylcotarnine hydrochloride.
2:30 P.M.	104.0	104.6	104.6	105.2	104.2
3:00	103.3	103.5	104.3	104.6	103.8
3:30	103.0	102.8	103.4	104.7	104.0
4:00	103.0	103.0	103.6	104.8	104.1
4:30	103.0	103.1	103.6	104.8	104.2
5:00	103.0	104.1	103.7	105.3	104.3
5:30	102.8	104.2	104.2	105.4	104.0
6:00	103.0	104.0	104.4	105.4	103.9
6:30	103.0	104.0	104.0	105.5	104.0
7:00	103.0	104.2	104.2	105.7	103.9
7:30	103.0	104.4	104.2	105.2	103.8
8:00	103.0	104.7	104.3	105.0	103.8
8:30	102.1	104.8	104.2	105.0	103.8
9:00	102.1	104.6	104.1	104.9	103.8
10:00	102.0	104.0	103.8	103.6	103.8

TABLE V.

Effect of Injecting 2':4'-Dihydroxyphenylcotarnine Hydrochloride in the Ventral Lymph Sac of the Frogs.

Weight of the frog.	Dose per Kg.	Dose per 20g. body weight.	Actual dose.	Result.
20 g.	0.10 g	2 g.	0.0020 g.	No effect.
30	0.10	2	0.0030	do
40	0.10	2	0.0040	Respiration slowed.
40	0.10	2	0.0040	No effect.
30	0.15	3	0.0045	do.
15	0.15	3	0.0023	do
30	0.15	3	0.0045	Respiration slowed.
25	0.15	3	0.0037	No effect.
25	0.20	4	0.0050	Recovered.
15	0.20	4	0.0024	do
27	0.20	4	0.0054	Recovered.
15	0.20	4	0.0030	do
40	0.25	5	0.0100	do
45	0.25	5	0.0105	do
30	0.25	5	0.0075	Dead in 20 hrs.
25	0.25	5	0.0065	Recovered.
20	0.25	5	0.0050	do
12	0.25	5	0.0030	Dead in 7 hrs.
55	0.35	7	0.0192	Dead in 5 "
25	0.35	7	0.0087	Recovered.
30	0.35	7	0.0105	Dead in 5 hrs.
35	0.35	7	0.0193	Dead in 6 hrs.

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Temperature Coefficients of Photochemical Reactions.

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In several publications from these laboratories (Mukherji and Dhar, *J. Phys. Chem.*, 1929, **33**, 850; Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **176**, 373; *J. Indian Chem. Soc.*, 1929, **6**, 143; Verma and Dhar, *Z. anorg. Chem.*, 1929, **184**, 90; Bhagwat and Dhar, *Z. anorg. Chem.*, 1931, **197**, 23; Malaviya and Dhar, *Z. anorg. Chem.*, 1931, **199**, 400), it has been shown experimentally that the temperature coefficient of a photochemical reaction is always less than that taking place in the dark. Moreover, it has been observed with numerous photochemical reactions taking place in radiations of different wavelengths that the temperature coefficient of a reaction depends on the acceleration of the reaction on illumination. The greater the acceleration of a reaction in light, the smaller is the value of its temperature coefficient. It has been emphasised in our publications that the influence of temperature, of light and of a positive catalyst on a reaction appears to be identical.

In this communication we shall deduce a relation by which the temperature coefficient of a photochemical reaction can be predicted from the temperature coefficient of the dark reaction and its photochemical acceleration at a definite temperature. Moreover, we shall critically examine certain views expressed in recent years correlating velocity and temperature of a photochemical reaction.

Arrhenius (*Z. phys. Chem.*, 1889, **4**, 226) formulated the following empirical relation for the velocity coefficient of a thermal reaction at two temperatures from considerations based on the existence of active and inactive molecules in a system.

$$K_{t_2} = K_{t_1} e^A$$

Marcelin (*Compt. rend.*, 1913, **157**, 1419; 1914, **158**, 116, 407; *Ann. Physique*, 1915, ix, **3**, 120), and Rice (*Brit. Assoc. Rep.*, 1915, p. 827) by applying statistical mechanics arrived at the same conclusion.

The influence of light on a reaction appears to be similar to that of temperature on the same reaction and consists in increasing the

number of active molecules. Hence it is possible to connect the amount of activation or acceleration due to light in terms of temperature effect. Assuming that the intensity of light remains the same when the temperature is varied, the photochemical effect in terms of temperature remains constant. Thus from the knowledge of the dark velocity coefficient and the photochemical acceleration at one temperature, it is possible to calculate the photochemical velocity coefficient at any other temperature. Moreover the thermal temperature coefficient can directly be connected with the photochemical temperature coefficient.

Let K_1 be the dark velocity coefficient at temperature T_1 , and K_2 be the dark velocity coefficient at temperature T_2 where $T_2 - T_1 = 10$.

Let K'_1 be the light velocity coefficient at temperature T_1 (all temperatures are expressed in absolute scale), then

$$K_2 = K_1 e^{A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \text{or} \quad A = \frac{T_1 \cdot T_2 \log x}{10} \quad \text{where} \quad x = \frac{K_2}{K_1}$$

$$\text{also } \log \frac{K'_1}{K_1} = \log y = A \left(\frac{T_x - T_1}{T_1 \cdot T_x} \right)$$

where T_x is the temperature of the dark reaction corresponding to the photochemical velocity coefficient K'_1 , then

$$T_x = \frac{T_1 \cdot T_2 \log x}{T_2 \log x - 10 \log y}$$

Hence the photochemical acceleration corresponds to the rise in temperature

$$T_x - T_1 = \frac{10 T_1 \log y}{T_2 \log x - 10 \log y}$$

Therefore the photochemical velocity coefficient at T_2 is equal to the dark velocity coefficient at $T_2 + T_x - T_1$.

$$\text{Thus} \quad K'_2 = K_2 e^{\frac{T_1^2 \log x \cdot \log y}{T_1^2 \log x - 10^2 \log y}}$$

$$\text{and} \quad K'_1 = K_1 e^{\log y}$$

Hence the temperature coefficient of a photochemical reaction

$$= \frac{K'_2 - K_2}{K'_1 - K_1} = \frac{K_2}{K_1} \left(\frac{e^{\log m} - 1}{e^{\log y} - 1} \right) \quad \text{where } \log m = \frac{T_1^2 \log x \log y}{T_2^2 \log x - 10^2 \log y}$$

where $\frac{K_2}{K_1}$ is the dark temperature coefficient.

The applicability of this relation has been tested by modifying this equation. When the photochemical acceleration is small, $10^2 \log y$ can be neglected compared to $T_1^2 \log x$. Hence $\log m = \frac{T_1^2}{T_2^2} \log y$. The equation can be written as

$$\frac{K'_2 - K_2}{K'_1 - K_1} = \frac{K_2}{K_1} \left(\frac{e^{\frac{T_1^2}{T_2^2} \log Ky} - 1}{e^{\log y} - 1} \right)$$

and the value of K can be calculated when we know both the temperature coefficients of the dark and photochemical reactions. If the value of K is unity it is clear that the equation holds good. It has been observed that for small accelerations in case of numerous reactions and for various wavelengths the value of K varies from 0.97 to 1.01. This relation has been found to be applicable to the following photochemical reactions: Sodium malonate and iodine, potassium oxalate and bromine, citric acid and potassium permanganate, bleaching of dicyanin, sodium formate and iodine, chromic acid and oxalic acid, sodium formate and mercuric chloride, sodium potassium tartrate and bromine, quinine sulphate and chromic acid, potassium permanganate and oxalic acid, sodium lactate and iodine, sodium tartrate and iodine and many other reactions. This relation holds good when the photochemical acceleration is small, but appears to be inapplicable in some cases where the photochemical acceleration is very high.

The equation

$$\frac{K'_2 - K_2}{K'_1 - K_1} = \frac{K_2}{K_1} \left(\frac{e^{\frac{T_1^2 \log x \log y}{T_2^2 \log x - 10^2 \log y} - 1}}{e^{\log y} - 1} \right)$$

shows not only that smaller the photochemical acceleration over the dark reaction, the greater is the photochemical temperature coefficient, but it also shows that it approaches the dark temperature coefficient more and more and in the limit it is equal to it and can never be greater than the dark temperature coefficient.

It follows from the law of photochemical equivalence first enunciated by Einstein that the temperature should have no effect on the velocity of photochemical reactions. In deducing this law, Einstein has made the assumption that all the molecules in a system possess the same amount of energy and are in the same state of activation. It is clear from Maxwell's law of distribution that all molecules can not possess the same amount of energy. Moreover, the kinetic energy of the molecules increases with temperature. It appears, therefore, that Einstein's law of photochemical equivalence cannot explain the observed temperature coefficient of photochemical reactions.

In order to explain the influence of temperature on the velocity of a photochemical reaction, it is generally assumed that molecules which have absorbed a quantum of light of stated frequency are often only activated if they already possess, before absorption, energy greater than a critical limit. If we represent by ' e ' the critical increment, that is, the amount of energy which must be given to a molecule to render it chemically active, the thermal acceleration of the reaction taking place in the dark is given by

$$\frac{d \log K}{dT} = \frac{Ne}{RT^2}$$

In order that a molecule can be brought into active state by a quantum of light, its energy must exceed the molecular energy by at least $e - h\nu$. The velocity of the thermal acceleration of the photochemical reaction is thus expressed by the equation

$$\frac{d \log K}{dT} = \frac{N(e - h\nu)}{RT^2}$$

According to this formulæ the thermal acceleration is less for the photochemical reaction than for the same reaction carried in the dark. Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285) has come to the conclusion that the temperature coefficient of a photochemical reaction is unity when the average energy of the reacting system is the same as the average energy of the reacting molecules and this

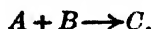
is actually the assumption made by Einstein in deducing his law of photochemical equivalence.

Recently A. Berthoud (*Trans. Faraday Soc.*, 1931, 27, 486) from considerations based on the limiting energies of molecules obtainable by integrating Maxwell's formulæ, has taken objection to the above equation, because it leads to the view that the velocity of a reaction ought to increase very rapidly with the frequency and to become independent of frequency after a limiting value of the frequency. But this is not supported by experimental results. In almost all photochemical reactions, increase of the quantum yield is observed in a very wide spectral zone with increase of frequency.

Bodenstein (*Z. Phys. Chem.*, 1913, 85, 318) suggested that for the occurrence of a photochemical reaction, it is necessary to have not only the activation of light absorbing component of the reacting system but also an activation of the other reactant is essential. According to Bodenstein this activation should be possible by the energy of the thermal agitation. Hence the photochemical reaction taken as a whole becomes sensitive to changes of temperature. It is clear from the above view of Bodenstein that the temperature coefficient of a thermal reaction should be higher than that of photochemical reaction, because in the thermal reaction the activation of both the reactants is due to the supply of thermal energy.

It is difficult to conceive that out of two types of reacting molecules, one type only will be affected by increase of temperature. It seems more plausible to assume that the amount of energy absorbed by one type of molecules is different from that taken up by the other.

Let us consider a reaction of the type.



Let us assume the amount of light taken up by the two types of molecules to be different and K_a and K_b the energies absorbed where $K_a + K_b = A'$ the total light absorbed by the reacting system. Let the energy due to temperature $T_1 = x + y$ of which x is the amount taken up by A type of molecules and y by B type of molecules. Let s be the energy due to temperature T_2 , then $\frac{sx}{x+y}$ will be taken by A type of molecules and

$\frac{sy}{x+y}$ will be taken by the B type of molecules.

If v_1 and v_2 are the dark velocity coefficients corresponding to the temperatures T_1 and T_2 and v'_1 and v'_2 are the photochemical velocity coefficients for the same temperature, then the

temperature coefficient of the thermal reaction $= \frac{v_2}{v_1} = \left(\frac{s}{x+y} \right)^2$

and the temperature coefficient of the photochemical reaction is given by

$$\frac{v'_2 - v_2}{v'_1 - v_1} = \frac{K_a \cdot K_b \cdot (x+y) + K_a \cdot y \cdot s + K_b \cdot s \cdot x}{(K_a \cdot K_b + K_b x + K_a y)(x+y)}$$

This is maximum when either K_a or K_b is equal to zero, and the

above equation becomes $\frac{v'_2 - v_2}{v'_1 - v_1} = \frac{s}{(x+y)} \dots (i)$

Hence the photochemical temperature coefficient is always less than the square root of the dark temperature coefficient. If $K_a = K_b$ we get

$$\frac{v'_2 - v_2}{v'_1 - v_1} = \frac{A' + 2x}{A' + 2(x+y)} \dots \dots \dots (ii)$$

This value of the temperature coefficient is less than (i). When a reaction is studied in almost monochromatic light, we actually observe the validity of the equation (i) and hence we may conclude in such cases that in this particular wavelength only one type of molecules is affected. The validity of equation (ii) is observed in reactions studied in composite light. This is quite obvious because in composite light there are various wavelengths affecting all types of molecules present. If only one type of molecules be affected by light

and the other by temperature alone, then $\frac{v'_2 - v_2}{v'_1 - v_1} = \frac{v_2}{v_1} =$ the

dark temperature coefficient. This however, is not supported by experimental observations. Hence the assumption of Bodenstein that only one type of molecules is activated by temperature and the other only by light seems incorrect.

Very recently Young and Style (*Trans. Faraday Soc.*, 1931, 27, 494) have advanced the view that the increase in the extinction coefficient with temperature is one of the causes of the temperature coefficient of quantum yield. Dhar and his co-workers

have actually observed that the extinction coefficient increases with temperature. But this can not be the cause of increased quantum yield with temperature. Contrary to the statement of Young and Style, (*loc. cit.*) Bhattacharya and Dhar (*loc. cit.*) have shown that the quantum yield falls with the increased absorption. This will be clear from some of their results given below :—

No.	Source of light.	Reaction mixture.	Temp.	Diameter of aperture of the iris-diaphragm in cm.	Quantum yield.
1.	1000 watt lamp	20% Cane sugar (15 c.c.) and $\frac{N}{20}$ HCl (5 c.c.)	35°	2	16.5×10^3
•	0.8	19.2×10^3
2.	4725 Å	$\frac{N}{101.7}$ Br and 43% methyl alcohol (10 c.c. each)	20°	2	6.2
			..	0.8	7.9
3.	4725 Å	$\frac{N}{113.7}$ Br and 25% ethyl alcohol (10 c.c. each)	20°	2	3.2
	0.8	4.6
	4725 Å	49% Acetone (5 c.c.) $\frac{N}{50}$ iodine	31°	2	41
	..	(10 c.c.) and $\frac{N}{9.42}$ HCl (5 c.c.)	..	0.8	53

Similar decrease of quantum yield with increase of light intensity has been observed with several other photochemical reactions.

The foregoing results show that the quantum yield decreases as the amount of light falling on the reacting mixture is increased. It has been observed that the amount of absorption is directly proportional to the amount of the incident radiation. Hence we can conclude that greater the intensity, the less is the quantum yield. The reason of this decrease in quantum yield with increased absorption of intensity is not far to seek. In a paper (*Z. anorg. Chem.*, 1931, 199, 406) concerning the relation between light intensity and velocity of photochemical reactions, we have shown that the amount of activation for the same increase of intensity or absorption falls as the intensity or absorption is increased and hence the amount of reaction per unit of absorption or quantum yield falls as the absorption or intensity increases. Thus the conclusion of Young and Style that

increased absorption with rise of temperature is one of the causes of increased quantum yield seems to be incorrect. The fact that the photochemical temperature coefficient is partially governed by the thermal one indicates that the mechanism of the photo-reaction is more or less allied to that of the dark reaction, although the increased light absorption with temperature increases the internal energy and chances of collision and thus the mechanism of the photo-reaction may be modified.

Summary.

The temperature coefficient of a photochemical reaction can be calculated from the temperature coefficient of the dark reaction and its photo-acceleration at a definite temperature.

Tolmgn's conclusion that the temperature coefficient of a photochemical reaction is unity when the average energy of the system is the same as the average energy of the reacting molecules, is inherent in Einstein's deduction of the photo-equivalence law.

Bodenstein's suggestion that out of two reacting molecules only one type of reacting molecules is activated by absorption of light and the other type by temperature only leads to conclusion unwarranted by experiments.

Increased light absorption with increase of temperature cannot be the cause of the increased quantum yield with increase of temperature. Results obtained in this laboratory show that the increase of light absorption leads to a decrease of the quantum yield and this can be satisfactorily explained from our view point that the number of molecules available for activation by light absorption decreases with increased absorption.

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Diamagnetism in Evidence of I. P. of Niton.

BY SUSIL CHANDRA BISWAS.

By using an apparatus almost similar to that used by Hertz and Kloppe in determining the ionisation potentials of rare gases, Holweck and Wertenstein (*Nature*, 1930, 126, 433) determined the I.P. of niton. Their method was to neutralise the negative space charge by accelerated positive ions from a subsidiary cathode. The quantity of niton used in their tube was of the order of 300 milli-curies, giving an effective pressure of about 0.8 bar. At such low pressures, the number of ions produced by α -rays was negligibly small and thus it was believed that the gas behaved like any other permanent gas. They indicated I. P. for niton at 10.6 volts. Kasmussen (*Z. Physik*, 1930, 62, 7, 494) examined the spectral relations of the radium emanation in a discharge tube with admixtures of He, Ne, and A. With He and Ne mixtures, only the spark spectra appeared while with A-mixture, only the arc spectra were noticed. The lines of the arc spectrum were arranged in series and a number of strong terms and two resonance lines were noted. From this the series limit computed was $P_0 = 10.7$ volts. Evidently the process involved in this mode of excitation is due to a collision of the second kind which means that the reaction takes place between the radium emanation and the excited A atom raised to its metastable state (11.7 volts) or to its ionised state (15.5 volts); the more probable energy state to which niton is raised is to be determined by the close resonance between the energies of the exciting and the excited states. It is thus not altogether unlikely that I. P. of Niton is greater than that of xenon whose ionisation voltage lies at about 11.5 volts.

By a comparison of the ionisation values of a number of elements whose outermost electrons belong to N, O, and P-shells, it was shown (Biswas, *Phil. Mag.*, 1928, vii, 3, 1091) that the contiguous elements of same chemical family (iso-electronic elements) having outer N, O, and P-shells diminish in their ionisation values due to an increase of shells from N to O-shell but then suddenly increase again for the corresponding elements having outer P-shell. From the beginning of the P-shell with one outer electron in Au (79) to the addition of 5

electrons in Bi (83), i. e., (to the addition of 3 electrons in $6s$ group after the completion of the subgroup $6p$ with two outer electrons) the rise in ionisation values of all the elements having outermost P-shell from the corresponding iso-electronic elements having outermost O-shell was unmistakably noticed.

TABLE I

N-shell		O-shell		P-shell.	
Cu	7.69	Ag	7.54	Au	9.25
Zn	9.35	Cd	8.95	Hg	10.39
Ga	5.97	In	5.76	Tl	6.78
Ge	7.85	Sn	7.38	Pb	7.93
As	9.40	Sb	8.0	Bi	8.0 ± 0.5
Kr	13.8	Xe	11.5	Nt	14.0 ± 0.5

Now the relation that has been found to hold so far till Bi, can surely be extended to the completion of the sub group $6s$ in niton (86) and thus it is expected that the I. P. of Nt should be greater than that of xenon. Ionisation values of the iso-electronic elements having successively the outer shells L, M, N, O, etc, fall off regularly and continuously till the elements having outer O-shells are reached. Thus keeping aside the elements having outer P-shell the gradual diminution of the ionisation values with the increase of the number order of the shell is a common feature, which in no case has however been extended for any known I. P. of an element having its outer electron in P-shell (shells $1s$ to $5d$ completed with, 78 electrons) and thus the extension of the relation that has subsisted among the rare gases from He till Xe, to Niton does not carry any weight.

It is proposed to argue on the evidence of the diamagnetic susceptibility that the elements having outer P-shell behave abnormally with respect to those having any other outer shell. L. Pauling (*Proc. Roy. Soc.*, 1927, A, 114, 181) has obtained a formula for the diamagnetic susceptibility of a number of free atoms and ions.

$$\chi_a = -2.01 \times 10^{-6} \sum_k \frac{n_k^4}{(Z - S_{M_k})^3} \left[1 - \frac{\{3l_k(l_k + 1) - 1\}}{5n_k^2} \right]$$

in which χ_a = diamagnetic susceptibility for the atom, n , the total quantum number, $l = (k - 1)$, k being the old azimuthal quantum

number, Z =nuclear charge, Sm_s =screening constant for diamagnetism, \sum_s means that the summation extends over all electrons in the atom.

Specific susceptibilities per unit mass calculated by this equation are given below for the elements having outer N, O and P-shells.

TABLE II

$$-\chi \times 10^8.$$

N-shell		O-shell		P-shell	
Cu	21 (18)	Ag	41 (20)	Au	33 (15)
Zn	17 (15)	Cd	33 (18)	Hg	28 (15)
Ga	14 (24)	In	30 (11)	Tl	24 (24)
Ge	12 (12)	Sn	23 (35)?	Pb	17 (12)
As	10 (31)?	Sb	20 (82)	Bi	18 (140)
Kr	37	Xe	44	Nt-41 (I.P.=10.6 volts) 32(I.P.=14 ± 0.5 volts)	

Clearly enough the specific susceptibilities for all the elements having outer O-shell increase in values from the corresponding elements having outer N-shell but these values decrease again for the elements of the same iso-electronic series having outer P-shell. It will thus be noticed that the relation with diamagnetism and ionisation voltages for the elements under different shells act exactly in opposite senses. It is thus believable that the specific susceptibility increases continuously for rare gases with the increase of the order of the shell till the outer O-shell is completed in xenon but diminishes again to a value even less than that of xenon with the increase of the next outer P-shell in niton.

Specific susceptibilities determined experimentally by Honda and Owen, in the metallic states of these elements are included within brackets in Table II, to show that the relation brought out by these values are quite in keeping with those calculated according to Pauling. Of these experimental values, those for In and As are doubtful due to impurities. Susceptibilities of Sb and Bi are already known to be abnormally high. Hence the values for Sb and Bi could not necessarily be fitted in the chart. These high values for Sb and Bi are possibly due to the fact that besides the effect of the electrons bound with the atom core (Pauling's χ values for Bi=18 × 10⁻⁸) the influence of the free conducting electrons and the influence of the

bindings of the crystal lattices play important parts to enhance in values.

Since diamagnetic susceptibilities primarily depend on the number of outer electron group, the mean susceptibility of the rare gas atoms-Kr, Xe, and Nt has been only approximately calculated for the electrons associated with (n, k) orbits orientated at random by evaluation of the quantum numbers of Pauling's equation with the assigned values of the group, while their effective charges have been only roughly eliminated by the values of the Ionisation Potentials corresponding to the removal of an electron of that group (Stoner, "Magnetism," p. 28). These values are included in Table II. It shows that χ for Nt is lower than that of xenon for both the values of I. P. of 10.6 and 14.0 ± 0.5 volts. For Kr, Xe, and Nt contributions due to the inner electron groups than the outer-most ones are not taken into account, hence these values are found much more reduced than Pauling's values for the same elements. Dia-magnetic susceptibility of Kr, Xe and Nt has also been calculated (Biswas, *Phys. Rev.* 1981, 38, 1784) according to Slater's method of charge distributions of the different electron shells in which the total quantum numbers of N, O, and P-shells have been substituted by their effective quantum numbers of 3.7, 4.0, and 4.5 respectively Slater, *Phys. Rev.*, 1930, 36, 57). This method gives a very low value of χ_s for Nt (-46.6×10^{-6}) which seems to support a lower χ value of niton.

Nielsen (*Nature.*, 1930, 18, 620) by a study of the spectroscopic data of Rasmussen (*loc.cit.*) has estimated the radial charge distributions of Nt according to Hartree's method of self consistent field. This offers another independent mode of checking χ for Nt which is proposed.

Incidentally it may be remarked here that the distinctive feature as exhibited by the elements having their outer-most electrons in P-shell as apart from the sequence that holds with the increase of the order of the shell till O-shell is completed, is seen to arise as due to the evaluation of the quantum numbers and the effective charges corresponding to their (n, k) group.

The Reduction of Ferric Chloride by Citric Acid, Malic Acid and Sugars.

BY RUKMINI MOHAN PURKAYASTHA.

The reduction of ferric chloride by mandelic acid, lactic acid and tartaric acid was published in a previous paper (*J. Indian Chem. Soc.*, 1929, 6, 827). A large amount of work has already been done on the reduction of ferric chloride by organic acids and of ferric salts of organic acids (Benrath, *Z. Phys. Chem.*, 1919, 74, 115; Bolin, *Z. Phys. Chem.*, 1914, 87, 490; Allmand and Young, *J. Chem. Soc.*, 1931, p. 3079)

These reactions are characterised by their simplicity. The dark reaction and the temperature coefficient are generally very small and the photochemical reaction is zero molecular. The present paper deals with the reduction of ferric chloride by citric acid, malic acid, glycerine and some sugars, such as glucose, mannose, galactose and laevulose.

The source of light was a quartz-mercury burner. The reactions were studied at 435μ and 366μ . These monochromatic radiations were obtained by means of filter Nos. 22870 and 312 of Schott and Gen. The intensity of radiation absorbed was measured as before by means of a Moll thermopile and Moll galvanometer and compared with the intensity of a standard Hefner. Other experimental arrangements were the same as before. Some of the substances, such as citric and malic acids used in these experiments, were all recrystallised but the sugars were used as such without crystallisation. They were preparations of Pfanstiehl Chemical Co. and of high grades of purity.

It was shown in our previous paper that addition of some hydrochloric acid is necessary in order to prevent the disturbing influences due to the hydrolysis of ferric chloride and dissociation of hydrochloric acid produced in course of the reaction. On account of very large absorption in blue and violet region, even a considerable variation in hydrochloric acid concentration did not affect the velocity of reaction appreciably. In the present case, concentration of hydro-

chloric acid has been kept equal to that of ferric chloride, 2 C.c. of the reaction mixture was always titrated with nearly 0.008N thiosulphate solution.

TABLE I.

485 $\mu\mu$.FeCl₃, 0.03M. HCl, 0.08M Citric acid, 0.25M. Temp., 30°.

Time in hrs.	0	1.25	2.5	3.75	5
(a-x)	19.2	16.15	13.1	10.1	7.15
x/t		2.44	2.44	2.4	2.36

Glucose, 0.25M.

Time in hrs.	0	1.25	2.5	3.75	5
(a-x)	19.35	18.25	17.15	16.1	15.05
(x/t)		0.88	0.88	0.84	0.84

Lævulose, 0.25M.

Time in hrs.	0	1.25	2.5	3.75
(a-x)	19.2	17.95	16.85	15.85
x/t		1.0	0.88	0.8

TABLE II.

Glucose, 0.25M. 366 $\mu\mu$.

Time in hrs.	0	2	4	6
(a-x)	19.3	18.55	17.8	17.05
x/t		0.375	0.375	0.375

It will be seen that except in the case of lævulose, the reactions are zero-molecular. Galactose also showed a similar fall in the value of x/t . In the case of malic acid, mannose and glycerine, truly zero-molecular constants were obtained. The dark reaction was measured in all cases and found to be exceedingly small. Lævulose however showed appreciable dark reaction which is given in Table III.

TABLE III.

Lævulose, 0.25M. FeCl₃, 0.03M. HCl, 0.08M. Temp., 30°.

Time in hrs.	0	24	48
(a-x)	19.3	17.75	15.3

TABLE IV.

Influence of Intensity.

	435 $\mu\mu$ Energy absorbed 1860 ergs. x/t	Energy absorbed 950 ergs. x/t	366 $\mu\mu$ Energy absorbed 480 ergs. x/t	Energy absorbed 230 ergs. x/t
0.25M-Citric acid	2.43	1.3	0.75	0.38
0.25M-Malic acid	1.3	0.7		
	Energy absorbed 1220 ergs.	Energy absorbed 910 ergs.		
0.25M-Glucose	0.86	0.44	0.375	0.18
0.25M-Galactose	0.88	0.43		

The above table shows that for each frequency of radiation, the reaction velocity is directly proportional to the energy absorbed.

TABLE V.

Influence of Concentration of Ferric Chloride.

HCl, 0.08M.

Temp. 30°

	x/t		(435 $\mu\mu$)		x/t (366 $\mu\mu$)	
Conc. of FeCl ₃ ...	0.08 <i>M</i>	0.03 <i>M</i>	0.015 <i>M</i>	0.08 <i>M</i>	0.03 <i>M</i>	0.015 <i>M</i>
0.25 <i>M</i> -Citric acid	2.45	2.43	2.3	0.75	0.74	0.74
0.25 <i>M</i> -Malic acid	1.3	1.25	1.25		0.67	0.65
0.25 <i>M</i> -Glucose		0.088	0.065	0.38	0.375	0.37
0.25 <i>M</i> -Mannose		0.87	0.66		0.35	0.35

It will be seen that the reaction velocity remains practically the same even with fairly wide variation in the concentration of ferric chloride. With glycerine and sugars, however at 435 $\mu\mu$, the value of x/t increased with increase in the concentration of ferric chloride. Intensity measurements showed that the incident 366 $\mu\mu$ was completely absorbed in all cases. The incident 435 $\mu\mu$ was also completely absorbed by the different mixtures of organic acids and ferric chloride but in the case of mixtures of sugars and ferric chloride with 0.08M-FeCl₃, the absorption was 1220 ergs and with 0.015M-

FeCl_3 solution it was 910 ergs, the values of x/t being 0.87 and 0.65 respectively which are exactly proportional to the energy absorbed. The zero-molecular constants, obtained at $485\mu\mu$ in the case of sugars and glycerine though the incident radiation was not at all completely absorbed, are due to the fact that owing to very small velocity, only 15 to 20 per cent. transformation was measured and within this small change in the concentration of ferric chloride there was no appreciable variation in the energy absorbed.

TABLE VI.

Quantum Efficiency.

Reaction Cell: 4 cm. \times 4 cm. \times 0.5 cm.

Ferric chloride, 0.03M. HCl, 0.03M. Temp., 30°.

Amount of FeCl_3 , reduced per hr. in c.c. of 0.0082N-thiosulphate solution per 2 c.c. reaction mixture.

	435 $\mu\mu$	366 $\mu\mu$
	Energy absorbed, 1860 ergs.	Energy absorbed, 480 ergs.
Citric acid, 0.25M	2.48	0.75
Malic acid, ..	1.25	0.45
	Energy absorbed 1220 ergs.	
Glucose, 0.25M	0.86	0.37
Mannose, ..	0.87	0.355
Lævulose, ..	0.88	0.36
Galactose, ..	0.87	0.37
Glycerine, ..	0.68	0.35

Citric acid and ferric chloride at 366 $\mu\mu$.

$$\text{Energy absorbed} = \frac{480 \times 366 \times 10^{-7} \times 16}{6.55 \times 10^{-27} \times 3 \times 10^7} = 1.48 \times 10^{15}$$

$$\begin{aligned} \text{Mols of FeCl}_3 \text{ reduced} &= \frac{0.75 \times 0.0082 \times 6.1 \times 10^{23} \times 8}{2 \times 1000 \times 60 \times 60} \\ &= 1.68 \times 10^{15} \end{aligned}$$

$$\frac{\text{Mols. transformed}}{\text{No. of quanta absorbed}} = \frac{1.68 \times 10^{15}}{1.48 \times 10^{15}} = 1.14.$$

TABLE VII.

Showing the number of mols of FeCl_3 reduced per quantum of energy absorbed with different reductants.

	485 $\mu\mu$	366 $\mu\mu$		485 $\mu\mu$	366 $\mu\mu$
Citric acid	0.8	1.14	Laevulose	0.46	0.55
Malic acid	0.41	0.7	Galactose	0.44	0.55
Glucose	0.43	0.57	Glycerine	0.34	0.53
Mannose	0.44	0.53			

It was shown in our paper already referred to that with mandelic acid as reductant the number of mols of ferric chloride reduced per quantum of energy absorbed was between 1 and 1.8 and with lactic acid and tartaric acid as reductants between 0.45 and 0.8. Hence it may be said that with sugars, glycerine, lactic acid, tartaric acid and malic acid as reductants, about two quanta are necessary per mol of ferric chloride reduced; while with mandelic and citric acids, one molecule of ferric chloride is reduced per quantum of energy absorbed.

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Examination of the Oil of *Clupea Ilisha*.

BY M. GOSWAMI AND J. DATTA.

Clupea Ilisha is found abundantly in the rivers of Bengal and Burma. The output is so large that after supplying the entire rainy season, fishermen saltup the surplus to sell in winter when this variety of fish is scarce. In this salting process much of the oil comes out and as such is practically lost. With a view to finding out some technical utilisation of this oil the present work was undertaken.

The fish is very cheap in proper season. It yields about 20 per cent. oil on being simply boiled with saline water, retaining its shape if carefully handled.

The oil is characterised by its pale yellow colour, fat like consistency, slight fishy odour and low iodine value. In all these properties the oil can be differentiated from marine fish oils.

An examination of the oil gave the following values.

Consistency and colour	Like butter fat.
Specific gravity at 23°	0.9194
Refractive index at 40°	1.4606
Saponification value	200.0
Iodine value	88.0
R. W. value	1.7
Polaneske value	0.77
Acid value	2.19
Unsaponifiable matter	•	0.85 p.c.

Though the oil contains a large proportion of linoleic acid together with clupanodonic acid (8 p.c.),⁷ the oil film when exposed to atmosphere for about a month, did not show any appreciable sign of drying, indicating thereby the non-drying character of the oil. The oil separates into its solid and liquid fractions on standing at a temperature of 30°. The solid fraction has a melting point of 46° and a setpoint of 36°, whereas the same for the liquid fraction are

21° and 10° respectively. The mixed fatty acids were examined and found to contain 37.4 per cent. solid acid and 56.3 per cent. liquid acids. The liquid acids were further separated by Bromide method and gave oleic acid, 57 p.c., linoleic acid, 35 p. c. and clupanodonic acid, 8 p.c., whereas the solid acid was almost entirely constituted of palmitic acid. The unsaponifiable matter was examined and was found to contain cholesterol. During the examination of fatty acids, a dirty mass having strong fishy odour was liberated when the dry soap obtained by saponifying the oil, was acidified with hydrochloric acid. It was practically insoluble in ether but dissolved easily in alkalis. As the quantity was very small it could not be examined further. The oil responded to the test for vitamin D and gave soft soap on saponification with caustic soda, both the properties are technically utilisable.

EXPERIMENTAL.

Examination of the Mixed Fatty Acids.

The oil was saponified with alcoholic potash and alcohol driven off. The dried soap obtained was first extracted with petroleum ether to remove unsaponifiable matter, then decomposed by dilute hydrochloric acid and the liberated fatty acid layer was washed free from mineral acids. It was examined and the following values were obtained.

Iodine value	90.5
Mean mol. wt.	268.5
Melting point	42°

The mixed fatty acids were separated into liquid and solid fractions by the method of Twitchell (*Ind. Eng. Chem.*, 1921, 13, 806), and the following results were obtained.

	p.c.	Iodine value.	M.p.
Solid acids	37.4	1.75	57°
Liquid acids	56.3	144.5	...

Examination of the Oil by Alcoholysis.

50 C.c. of the oil were submitted to alcoholysis using POCl_3 (Goswami and Ramanujam, *J. Indian Chem. Soc.*, 1931, 8, 418).

The resulting ester freed from acids, glycerine and moisture was distilled under 5 mm. pressure with the result given below.

Temperature.		Fractions.
Up to 170° Traces
170°—190° 17 c.c.
190°—212° 24 c.c.

A black residue having strong fishy odour remained undistilled even above 230°. Results of the distillation point out the following:

(a) Practical absence of lower acids. This is corroborated by low Reichert value.

(b) Presence of palmitic acid to the extent of 40 p.c. of the total acid. This has been supported by the separation of acid as given above and by the study of solid acid as is given hereafter.

Examination of the Solid Fatty Acid.

The solid fatty acid as obtained by separating the mixed fatty acid was esterified in methyl alcohol by passing a current of dry HCl gas. Ester obtained was a white liquid at ordinary temperature but solidified when cooled into plates, m. p. 26°. This was distilled under vacuum with the result given below.

Temperature.	Pressure.	Fractions.
Up to 170°	... 5 mm.	Traces
170°—190°	Entire content

From the result of the distillation it seems probable that the distillate is constituted of methyl palmitate.

The distilled ester was saponified by alcoholic potash and fatty acids liberated by hydrochloric acid. This was crystallised 5 times from absolute alcohol and the crystals gave m. p. 59° and molecular weight 268 corresponding figures for palmitic acid being 61° and 256. The lead salt was prepared and crystallised from alcohol melting at 109°; lead palmitate melts at 112°. It therefore seems probable that the solid acid is mostly constituted of palmitic acid.

Examination of Liquid Fatty Acid.

The liquid fatty acid as separated by Twitchells method was brominated in dry ethereal solution by bromine in presence of glacial acetic acid. Ether insoluble bromides being filtered off, the solution was washed with thiosulphate solution to remove excess of bromine. The residue obtained after distilling off the ether, was boiled with petroleum ether and cooled over night in an ice chest. The separated crystals were filtered and the mother liquor was little concentrated, then again cooled, when a second crop of crystals was obtained. The process was repeated thrice when no further crystals appeared. Results obtained are given below.

Bromide.	M. p.	Inference.
Insoluble in ether	Decomposes at 200°	Octabromide
Insoluble in ether but soluble in benzene		Hexabromide absent
Insoluble in petroleum ether	113°	Tetrabromide
Soluble in petroleum ether	Oil	Dibromide

From the above result it is evident that clupanodonic acid, linoleic acid and oleic acid are present in the oil. The percentages of the acids as given before were calculated from the amount of bromides.

Unsaponifiable matter.—The oil after saponification with caustic potash was extracted with petroleum ether from which its percentage was determined after evaporating off the solvent. The residue was crystallised from alcohol and crystals obtained were found to be those of cholesterol.

Vitamins.—Vitamin A was tested for by antimony trichloride (*Analyst*, 1928, 53, 156). There was no coloration at first but after a few minutes a violet colour developed which gradually turned into deep red. This is considered to be good colour reaction for vitamin D. But the absence of blue coloration at the beginning shows the absence of vitamin A. Vitamin D was further examined by Shears test (*Proc. Soc. Expt. and Biol. Medicine*, 1926, 23, 546.)

Friedel and Crafts' Reaction with Phenolic Acids.

BY P. C. MITTER AND HIRENDRA CHANDRA RAY.

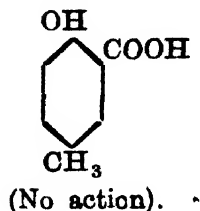
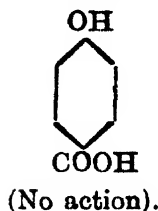
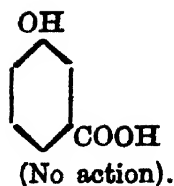
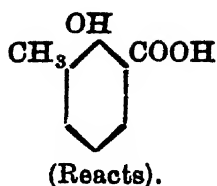
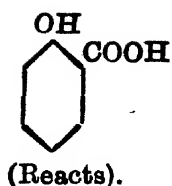
Although the occurrence, in nature, of hydroxyanthraquinone carboxylic acids like munjisthin, rhein, pseudopurpurin etc. is by no means rare, very few attempts appear to have been made for the direct synthesis of carboxylated benzoic acids from which such anthraquinone carboxylic acids could be obtained by ring-closure. Limpricht (*Annalen*, 1898, **303**, 274) condensed phthalyl chloride with hydroxybenzoic esters and obtained in the case of salicylic ester a benzoylbenzoic acid which he named phthalylsalicylic acid but he did not determine the constitution of the substance.

We have tried to condense phthalic anhydride with diverse phenolic esters in the hope that such a reaction would give substituted benzoylbenzoic acids, from which anthraquinone carboxylic acids could be obtained.

The condensation of salicylic ester with phthalic anhydride in acetylene tetrachloride medium, in presence of anhydrous aluminium chloride gave a product melting at 248°, identical with the phthalylsalicylic acid of Limpricht (*loc. cit.*). Now the condensation may have taken place either in *o*- or *p*-position to the hydroxyl group although as Ullmann and Schmidt (*Ber.*, 1919, **52**, 2098), have shown in the case of the condensation of phenols and phthalic anhydride in acetylene tetrachloride medium, condensation in *o*-position to the hydroxyl group was more probable.

To settle this question, several experiments were tried with various other hydroxy acids with the following results:

1. From *o*-cresotinic acid (methyl ester), a benzoylbenzoic acid was obtained having properties very similar to that obtained from salicylic ester.
2. *p*-Cresotinic ester, on similar treatment gave no reaction.
3. *p*-Hydroxybenzoic ester gave no reaction.
4. There was also no reaction with *m*-hydroxybenzoic ester.



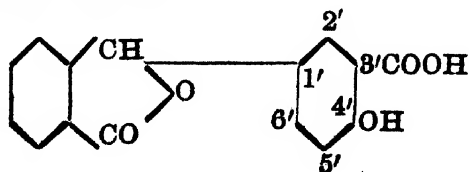
From the above it may be reasonably concluded that, under the conditions of the experiment, combination takes place only in *p*-position to a hydroxyl group but that no combination takes place in *o*-position to a hydroxyl or a carboxyl group.

Having thus determined the probable position of the link between the two benzene nuclei, we next attempted the closingup of the anthraquinone ring, with (4'-hydroxy-3'-carboxybenzoyl)-2-benzoic acid (I) as also with its methylation product but without success.

The preparation of the anthraquinone *via* anthrone was next thought of and for this purpose the acid (I) as also its methyl ether were subjected to the action of zinc dust and hydrochloric acid in acetic acid solution (Bistrzycki and Krauer, *Helv. Chim. Acta*, 1923, 6, 753). Several ring-closing experiments were tried with the reduction product but no anthraquinone was formed, the unchanged mother substance being obtained in every case.

On a careful examination of the reduction product it was found that a lactone had resulted by the partial reduction of the -CO- group to a -CHOH- group.

Reduction with zinc and caustic soda (Bistrzycki and Schepper, *Ber.*, 1898, 31, 2792), and also with zinc dust and ammonia in presence of copper sulphate (Scholl and Neovius, *Ber.*, 1911, 44, 1080), yielded the same lactone.



EXPERIMENTAL.

(3'-Carboxy-4'-hydroxybenzoyl)-2-benzoic acid, (I).—Powdered phthalic anhydride (10 g.) was mixed with methyl salicylate (10 g.) in a flask containing 50 c. c. of acetylene tetrachloride and finely powdered aluminium chloride (25 g.) gradually added to the mixture with frequent shaking. The flask was then heated on the water-bath for about 3-4 hours and finally on the oil-bath at 125° for a short time. The contents of the flask were then decomposed by adding ice and distillation in steam whereby acetylene tetrachloride and unchanged salicylic acid were removed. The crude acid thus obtained was dissolved in soda solution, filtered and precipitated with hydrochloric acid and further purified as the calcium salt and reprecipitated with hydrochloric acid. It crystallised from acetic acid in aggregates, m. p. 248°. (Found: C, 63·37; H, 3·44. $C_{15}H_{10}O_6$ requires C, 62·94; H, 3·49 per cent.). The substance is identical with the phthalylsalicylic acid of Limpricht (*loc. cit.*).

(3'-Carboxy-4'-methoxybenzoyl)-2-benzoic acid (II).—The acid (I) was methylated with dimethyl sulphate and caustic soda in the usual manner. Aggregates from acetic acid, m. p. 232°. (Found: C, 63·89; H 4·04. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent.).

Methyl-(3'-carbomethoxy-4'-hydroxybenzoyl)-2-benzoate (III).—The acid (I) was esterified with methyl alcohol and sulphuric acid in the usual manner. Rectangular plates from aqueous alcohol, m. p. 130-31°. (Found: C, 64·67; H, 4·46. $C_{17}H_{14}O_6$ requires C, 64·97; H, 4·46 per cent.).

Methyl-(3'-carbomethoxy-4'-methoxybenzoyl)-2-benzoate (IV).—This was obtained by esterifying (II). Rectangular plates from aqueous alcohol, m. p. 105-06°. (Found: C, 65·83; H, 5·03. $C_{18}H_{16}O_6$ requires C, 65·85; H, 4·88 per cent.).

(3'-Carboxy-4'-hydroxyphenyl)-2-phthalide (V).—The acid (I) (5g.) was dissolved in acetic acid (100 c. c.) and treated with extrafine zinc dust and after the gradual addition of hydrochloric acid (d 1·19, 10 c. c.) heated nearly to boiling for 6 hours. The mixture was filtered hot and carefully diluted with hot water. The precipitate was taken up with dilute soda solution, filtered and acidified with hydrochloric acid. It crystallises in plates from aqueous alcohol, m. p. 211-12°, yield about 3·5 g. (Found: C, 66·26; H, 3·89. $C_{15}H_{10}O_5$ requires C, 66·66; H, 3·70 per cent.).

(3'-Carboxy-4'-methoxyphenyl)-2-phthalide, (VI).—This was obtained by reducing (III) in the same manner as above. The phthalide melts at 164°. (Found: Eq. wt., 282; C, 67.37; H, 4.49. $C_{16}H_{12}O_5$ requires Eq. wt., 284; C, 67.60; H, 4.23 per cent.).

(3'-Carboxy-4'-hydroxy-5'-methylbenzoyl)-2-benzoic acid, (VII).—It was obtained in the same way as the corresponding salicylic ester condensation product on using *o*-cresotinic acid methyl ester. Yield about 13 g. from 10 g. of phthalic anhydride. It crystallises in aggregates from acetic acid, m. p. 258-61° (decomp.). (Found: C, 63.80; H, 4.04. $C_{16}H_{12}O_6$ requires C, 64.0; H, 4.0 per cent.).

Methyl-(3'-carbomethoxy-4'-hydroxy-5'-methylbenzoyl)-2-benzoate, (VIII).—It was obtained by esterifying the above in the usual manner, m. p. 103.04°. (Found: C, 65.61; H, 4.98. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.88 per cent.).

(3'-Carboxy-4'-methoxy-5'-methylbenzoyl)-2-benzoic acid, (IX).—It was obtained by methylating (VII) in the usual manner. Crystals from acetic acid, m. p. 197-98°. (Found: C, 64.57; H, 4.51. $C_{17}H_{14}O_6$ requires C, 64.96; H, 4.46 per cent.).

Methyl-(3'-carbomethoxy-4'-methoxy-5'-methylbenzoyl)-2-benzoate, (X).—It was obtained by esterifying (IX). Crystals from aqueous alcohol, m. p. 93°. (Found: C, 66.46; H, 5.41. $C_{19}H_{18}O_6$ requires C, 66.66; H, 5.26 per cent.).

(3'-Carboxy-4'-hydroxy-5'-methylphenyl)-2-phthalide, (XI).—It was obtained by the reduction of (VII) as in the case of phthalyl-salicylic acid. Flakes from aqueous alcohol, m. p. 204.05°. (Found: C, 67.29; H, 4.46. $C_{16}H_{12}O_5$ requires C, 67.60; H, 4.23 per cent.).

(3'-Carboxy-4'-methoxy-5'-methylphenyl)-2-phthalide, (XII).—It was obtained by the reduction of (IX) with zinc dust and hydrochloric acid in presence of acetic acid. Aggregates from aqueous alcohol, m. p. 160°. (Found: C, 68.22; H, 4.71. $C_{17}H_{14}O_5$ requires C, 68.46; H, 4.70 per cent.).

(3'-Carbomethoxy-4'-hydroxy-5'-methylphenyl)-2-phthalide, (XIII).—It was obtained by esterifying (XI) in the usual manner. Crystals from aqueous alcohol, m. p. 114-15°. (Found: C, 68.62; H, 4.89. $C_{17}H_{14}O_5$ requires C, 68.46; H, 4.70 per cent.).

Complex Compounds of Iridium. Part I.

Compounds with Organic Sulphides.

BY PRAFULLA CHANDRA RÂY AND NADIABEHARI ADHIKARI.

Iridium and platinum, placed as they are in the same group of transitional elements in the periodic table, show a remarkable similarity in their inorganic compounds as well as a gradation of properties thereto. Though the methods of preparations are different, they give the same type of chlorides, *e.g.*, iridium-monochloride, iridium dichloride, iridium trichloride, iridium tetrachloride and platinum mono-, di-, tri-, and tetrachlorides. Of these iridium mono- and dichlorides are unstable, whereas in the case of platinum, the mono-, and the trichlorides are not stable; as to the formation of complexes with alkali chlorides, iridium tri- and tetrachlorides unite to form M_3IrCl_6 and M_2IrCl_6 respectively whereas platinum di- and tetrachlorides yield M_2PtCl_4 and M_2PtCl_6 .

For some years past, Rây and his co-workers, in a series of papers have studied the action of alkyl mono- and disulphides on chloroplatinic acid and potassium chloroplatinate with interesting results. (*J. Chem. Soc.*, 1923, **125**, 133; *J. Indian Chem. Soc.*, 1925, **2**, 178; *ibid.*, 1926, **3**, 338; *ibid.*, 1927, **4**, 467; *ibid.*, 1928, **5**, 139; *Z. anorg. chem.*, 1929, **178**, 329; *ibid.*, 1930, **187**, 33; *ibid.*, 1931, **198**, 53; *ibid.*, 1932, **203**, 401.) The constitution of some of the compounds they obtained could be represented on the basis of Werner's theory while those of others did not come within its purview but the authors proved beyond doubt that the latter are of complex nature and their constitution should be represented as such. A more recent paper by Angell, Drew and Wardlaw (*J. Chem. Soc.*, 1930, p. 349) has established that the isomerism found in co-ordinate compounds of platinum is of a structural and not of a spatial nature. The present investigation was undertaken with a view to explore the above possibilities in the iridium compounds of organic sulphides and to examine how far they resemble the corresponding platinum compounds.

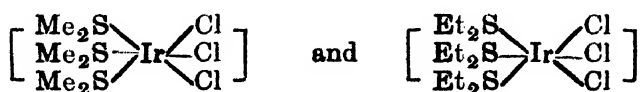
In this paper an account of the reaction of iridium tetrachloride with methyl sulphide, ethyl sulphide and diethyl disulphide has been described. The following compounds have been obtained:

- (1) $\text{IrCl}_3 \cdot 3\text{Me}_2\text{S}$ (4) $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$
 (2) $\text{IrCl}_3 \cdot 2\text{Me}_2\text{S}$... (6) $(\text{IrCl}_2)_2 \cdot 3\text{Et}_2\text{S}_2$
 (3) $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Me}_2\text{S}$ (5) $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Et}_2\text{S}$

In the case of platinum, no compounds of the type (1) or (4) were obtained but compounds of the type (2), (3) and (5), *e.g.*, $\text{PtCl}_3 \cdot 2\text{Et}_2\text{S}$, $\text{PtCl}_3 \cdot 2\text{Bz}_2\text{S}$ and $\text{Pt}_2\text{Cl}_5 \cdot 4\text{Bz}_2\text{S}$ have been isolated. $\text{PtCl}_3 \cdot 2\text{Et}_2\text{S}$, easily breaking up into $\text{PtCl}_2 \cdot 2\text{Et}_2\text{S}$ and $\text{PtCl}_4 \cdot 2\text{Et}_2\text{S}$, was proved to be a molecular compound but the other one $\text{PtCl}_3 \cdot 2\text{Bz}_2\text{S}$ resisted every attempt to break it up and was regarded

as an independent entity, being represented as $\left[\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Pt} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array} \begin{array}{c} \text{Bz}_2\text{S} \\ \diagdown \quad \diagup \\ \text{Bz}_2\text{S} \end{array} \right] \text{Cl}$

from its various reactions. The compound (2) is almost insoluble in all ionising solvents, and as it could not be split up into $\text{IrCl}_3 \cdot 2\text{Me}_2\text{S}$ and $\text{IrCl}_4 \cdot 2\text{Me}_2\text{S}$, it is better to represent it as a molecular compound $\text{IrCl}_3 \cdot 2\text{Me}_2\text{S}$. The compounds (1) and (4) can be represented thus

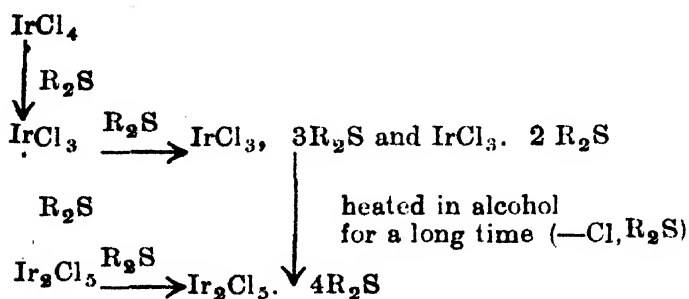


the co-ordination number of iridium being six. They are non-electrolytes, as is evident from the conductivity measurement in acetone (*vide experimental*). Such trivalent platinum compounds are totally non-existent.

Compounds (3) and (5) behave rather in a different manner from the corresponding platinum analogue $\text{Pt}_2\text{Cl}_5 \cdot 4\text{Bz}_2\text{S}$, which when recrystallised from hot alcohol breaks up into $\text{PtCl}_3 \cdot 2\text{Bz}_2\text{S}$ and $\text{PtCl}_2 \cdot 2\text{Bz}_2\text{S}$. But in the present case, the compounds are very stable and from the methods of their preparations, it appears quite unlikely that their constitutions are similar to those of the corresponding platinum compounds. The compound (5) although sparingly soluble in alcohol and acetone, separates in well defined crystals from boiling alcohol, the m.p. remaining the same even after two consecutive crystallisations.

The mode of reaction is the same as in the platinum series.

Irididium tetrachloride in presence of sulphides gradually loses chlorine, the reduction being more vigorous when heated in presence of alcohol.



As to the constitution of $\text{Ir}_2\text{Cl}_4 \cdot 3 \text{Et}_2\text{S}_2$, it can only be stated here that the disulphides are stronger reducing agents than the monosulphides and so in this case the reduction of iridium tetrachloride has proceeded a step further to iridium dichloride and it might be represented as $2(\text{IrCl}_2) \cdot 3 \text{Et}_2\text{S}_2$.

Had it been possible to arrest the above reactions stage by stage, the course and the mode of the formation of the different products could be further elucidated. The compounds (1) and (2) were the results of carrying on the reactions entirely in cold but when the same reaction was conducted on water-bath, (2) could not be isolated from the filtrate; only (3) was obtained and also an inseparable mixture containing a lower percentage of iridium (43.5) than both (2) and (3) but much higher than that of (1).

Iridium was estimated by slowly igniting the compound in a rose crucible and then reducing by hydrogen till the weight is constant and finally cooling the crucible in a current of carbon dioxide. This presented some difficulties as the compounds, (prepared from IrCl_4 supplied by Messrs. Schering-Kahlbaum) when reduced, sublimed and condensed in a very thin film on the lid and on the leading pipe. This film is insoluble in aqua regia, which, therefore, precludes the presence of rethenium and osmium but its weight is so small that it is not appreciable even after 6 or 7 operations.

The replacements of sulphides of these compounds by amines and ammonia are in progress and will be the subject of the next communication.

EXPERIMENTAL.

Preparation of $\text{IrCl}_3 \cdot 3\text{Me}_2\text{S}$.—To iridium tetrachloride (6g.),

di-methyl-sulphide (5g.) in alcohol (about 20 c.c.) was added and kept in closed conical flask with occasional shaking. The chloride dissolved completely in about 8 hours. After 24 hours the solution was heated under reflux on a water bath. After an hour a precipitate, yellow in colour, began to separate. The refluxing was stopped after 4 hours. The yellow precipitate was mixed up with a tarry mass which also came out during the above process. The entire mass was filtered hot and the filtrate concentrated in a vacuum desiccator. The residue was repeatedly extracted with hot alcohol and these extracts on concentration yielded yellow crystals, m.p. 228-230°, which on recrystallisation from warm alcohol melted at 238-39° (I); the insoluble residue—a grey coloured mass, was rather too small to be further purified for analysis. The main filtrate which was concentrated as indicated above, turned to a semisolid mass. It was then filtered under a strong suction and a crystalline substance was left behind. This was washed with a little alcohol and ether and finally recrystallised from warm alcohol (II) m.p. 238-39° with evolution of Me_2S but it did not break up into the metallic state as was also the case with the compound I. It is soluble in acetone and sparingly so in cold alcohol and benzene etc. Both products (I and II) were analysed and found to have the same composition. (Found: Ir, 40.89; Cl, 21.83; C, 14.30; S, 20.68. $\text{IrCl}_3 \cdot 3\text{Me}_2\text{S}$ requires Ir, 39.75; Cl, 21.93; C, 14.83; S, 19.79 per cent.).

Preparation of $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Me}_2\text{S}$.—The filtrate from the above was concentrated in vacuum to a tarry solid mass to which hot alcohol was added. Most of the tarry matter dissolved and a yellow substance was left behind. This was separated and the filtrate again evaporated in a vacuum, dissolved in hot alcohol. This process was repeated until the evaporated filtrate was completely soluble in alcohol without leaving any residue. The first crop and the next successive portions were found to be mixtures. The filtrate was then evaporated on water bath to dryness and the mass digested with boiling alcohol when a yellow substance separated out. This was refluxed with acetone on water-bath and filtered. The process was repeated till the acetone was almost colourless. It was finally washed with chloroform and ether—dried and analysed. It has got no m.p. and is very sparingly soluble in acetone, alcohol and other organic solvents. (Found: Ir, 47.90; Cl, 22.19; C, 11.28. $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Me}_2\text{S}$ requires Ir, 47.59; Cl, 21.88; C, 11.83 per cent.).

Second method of preparation.—When $\text{IrCl}_3 \cdot 3\text{Me}_2\text{S}$ was refluxed with alcohol and the solution together with traces of insoluble matter held in suspension, evaporated to dryness on water-bath and the process repeated 6—7 times, almost the whole of the substance became sparingly soluble in boiling alcohol and acetone. The undissolved portion was then collected, washed several times with hot alcohol and acetone and finally with ether and dried. It has no m.p. but gradually decomposes when heated above 200° . (Found: Ir, 47.41; Cl, 22.16 per cent.).

Preparation of $\text{IrCl}_3 \cdot 2\text{Me}_2\text{S}$.—Methyl sulphide (3.3 g.) in alcohol (20 c.c.) was added to iridium tetrachloride (4 g.) and the vessel kept closed. After 2 days a dirty precipitate began to separate out and this increased gradually up to the 4th day. To ensure complete reaction it was filtered off (after 7 days), the precipitate being digested with hot alcohol and acetone till the filtrate was almost colourless. The insoluble portion was too small to be further purified for analysis and was stored for investigation in future. The wash alcohol, on evaporation on water-bath to dryness, yielded a yellow substance, which on analysis (after purification) was found to be identical with the compound $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Me}_2\text{S}$. Three crops of a yellow substance were successively (I, II & III) obtained when the main filtrate was evaporated to dryness in a vacuum and subsequently digested with alcohol and the process thus repeated thrice. The alcoholic filtrate was next evaporated on water-bath to dryness and kept over it until the resulting black tarry mass became dull grey. This was lixiviated with hot alcohol when a yellow residue was left. It was washed with hot chloroform and alcohol to remove the last traces of the tarry matter. The filtrate obtained in this stage was too small for further investigation. The crops I and II were found to be impure but III and also the yellow precipitate obtained by evaporation on water-bath were found to be identical in composition. They have no sharp m.p. but decompose slowly above 200° . (Found: Ir, 45.36, 45.08; Cl, 24.92, 24.63; S, 15.59. $\text{IrCl}_3 \cdot 2\text{Me}_2\text{S}$ requires Ir, 45.57; Cl, 25.14; S 15.13 per cent.).

Preparation of $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$ and $\text{Ir}_2\text{Cl}_5 \cdot 4\text{Et}_2\text{S}$.— IrCl_4 (8 g.) and Et_2S (8 c.c.) in 50 c.c. alcohol were mixed together and refluxed for three hours. The mixture was then subjected to filtration when a very small amount of black residue remained behind. The filtrate on concentration in vacuum yielded a crystalline mass; it was collected and recrystallised from hot benzene in

which a very small portion—greyish white in colour—remained insoluble. It is soluble freely in benzene, chloroform and acetone and moderately so in alcohol and insoluble in water, m.p. 131° . (Found: Ir, 33.58; Cl, 19.01; S, 17.14; C, 26.02. $\text{IrCl}_3 \cdot 3 \text{Et}_2\text{S}$ requires Ir, 33.86; Cl, 18.68; S, 16.86; C, 25.28 per cent). The filtrate from the above on further concentration yielded a crop m.p. 194° (not sharp) which was too small for analysis. Finally the remaining tarry filtrate was evaporated to dryness on a water-bath and digested with alcohol, when a lemon yellow substance remained undissolved. This was collected, washed with benzene and chloroform in which it is sparingly soluble. The substance was dried and analysed, m.p. 207° . (Found: Ir, 42.06; Cl, 18.62; C, 19.23; S, 10.83. $\text{Ir}_2\text{Cl}_5 \cdot 4 \text{Et}_2\text{S}$, requires Ir, 41.82; Cl, 19.23; C, 20.80; S, 13.86 per cent). The above compound was also obtained when $\text{IrCl}_3 \cdot 3 \text{Et}_2\text{S}$ in alcohol, was refluxed for 30-35 hours; about 60% of the substance changed to $\text{Ir}_2\text{Cl}_5 \cdot 4 \text{Et}_2\text{S}$. It was then washed several times with hot benzene and acetone. (Found: Ir, 42.33 per cent.).

The Molar Conductivity of $\text{IrCl}_3 \cdot 3 \text{Et}_2\text{S}$ at Different Concentrations in Acetone at 25.5° .

TABLE I.

Molar conc.	0.008738	0.004369	0.002184	0.001092
Molar conductivity.	2.75	2.95	3.72	4.46

TABLE II.

Molar conc.	0.01281	0.00640	0.00320	0.00160
Molar conductivity.	2.59	2.77	3.02	3.36

Preparation of $(\text{IrCl}_2)_2 \cdot 3 \text{Et}_2\text{S}_2$.— IrCl_4 (2g.) in alcohol and Et_2S_2 (2g.) were mixed together and heated on water-bath under reflux. The chloride gradually dissolved and a deep red almost black liquid resulted. This was then evaporated on a water-bath with constant stirring till there was no evolution of hydrochloric acid. The solid tarry matter, thus obtained, was then triturated with alcohol when a yellow solid separated and a

deep red solution was left behind. The yellow substance was several times extracted with boiling alcohol when it almost completely dissolved and an orange yellow crystalline mass was obtained from the filtrate on cooling. The residue was small and could not be further purified. The main mother liquor (the above deep red solution) on concentration (1st and 2nd crop) in vacuum yielded an orange coloured crystalline substance identical with the preceding one and the succeeding crops gave anomalous analytical results. The substances were further purified by dissolving them in chloroform and precipitating with ether. It does not melt but gradually decomposes into the metallic state above 200° . (Found: Ir, 42.74; Cl, 15.06, 14.79; S, 21.66, 21.3. $\text{Ir}_2\text{Cl}_4 \cdot 3 \text{Et}_2\text{S}_2$ requires Ir, 43.17; Cl, 15.83; S, 21.47 per cent.).

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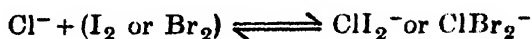
Received April 22, 1932.

On the Study of Polyhalides. Part I. Formation and Dissociation of Polyhalides of Hydrogen. (Chloro-dibromide, Chloro-diiodide, Bromo-diiodide, Tribromide and Triiodide of Hydrogen).

BY SUSIL KUMAR RAY.

Jakowkin (*Z. Phys. Chem.* 1896, **20**, 19) studied the dissociation of polyhalogen compounds of the type XI_3 , XBr_3 , XCl_3 , $XBrI_2$ (where X stands for Na, K, Li or $\frac{1}{2}$ Ba) and also that of HI_3 in aqueous solution with the aid of the distribution method. The dissociation of KI_3 and HI_3 in aqueous solution at different temperatures has also been investigated by Dawson (*J. Chem. Soc.*, 1901, **79**, 238). From a study of the solubility of Br_2 in aqueous solution of KBr, the formation of KBr_3 has been established by Worley (*J. Chem. Soc.*, 1905, **87**, 1107). Jones and Hartmann (*J. Amer. Electrochem. Soc.*, 1916, **30**, 295) have also proved, from measurements of equilibrium between Br_2 and water as well as between Br_2 and KBr solution at 0° that both KBr_3 and KBr_5 are formed in saturated solution. Mellor (*J. Chem. Soc.*, 1901, **79**, 225) has also studied the formation and dissociation of HCl_3 in aqueous solution by means of the solubility method. From the heat of solution of Br_2 in hydrochloric acid, Berthelot (*Compt. rend.*, 1815, **100**, 761) deduced the existence of the compound $HClBr_2$. By the spectroscopic method Job (*Ann. Chim.*, 1928, *x*, **9**, 148) has determined the dissociation constants of and the affinity values, for $KClBr_2$, $KClI_2$, $KBrI_2$, KBr_3 and KI_3 . A study of the formation and dissociation of HBr_3 by means of the distribution method has been made by Lewis and Storch (*J. Amer. Chem. Soc.*, 1917, **39**, 2501). Ray and Sarker (*J. Chem. Soc.*, 1922, **121**, 1449) has also studied the formation and dissociation of the polyhalides of hydrogen by the same method. They have shown that, by the interaction of a halogen acid (HCl or HBr) and a halogen (I_2 or Br_2), compounds of the type $HClI_2$, $HBrI_2$, or $HClBr_2$ are formed in solution. The above authors, from a calculation of the degree of dissociation, came to the conclusion that as the dissociation of these compounds increases with the diminution in the concentration of the

halogen acid they are incapable of independent existence in the absence of either the halogen acid or halogen ions. In the present paper the formation and dissociation of these polyhalides of hydrogen have been studied by the freezing point method, and the equilibrium constants of the reactions



and the heats of formation of the complexes ClI_2 , ClBr_2 and Br_3 have been calculated. It is shown that the formation of the polyhalogen compounds like HClI_2 , HClBr_2 , HBr_3 can be definitely established with the aid of the freezing point method, and in the case of HBrI_2 , HBr_3 and HI_3 the complex compounds have been isolated in the free state. Reference may here be made to the isolation of the hydrates of HIBr_2 , HIBrCl and of $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$ (Cremer and Duncan, *J. Chem. Soc.*, 1931, 1862-64; Hannay, *ibid.*, 1473, 26, 851; Cagliote, *Atti. R. Accad. Lincei*, 1929, 9, 563).

In the following experiments, the equilibrium constant has been calculated according to the formula $K = \frac{c}{ab}$, where K is the equilibrium constant; a , b and c are respectively the concentration of the free halogen ions (from the dissociation of the halogen acid), the free halogen, and the complex polyhalide ion. The values of a , b and c can be found out from the following relations:

$$a + c = \text{normality of the halogen acid} \times \text{its degree of dissociation},$$

$$b + c = \frac{\text{normality of the thiosulphate (employed for titration)} \times \text{the volume required}}{2 \times \text{volume of solution taken}}.$$

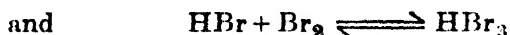
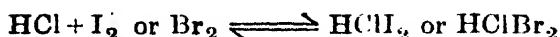
$$b = \frac{\text{wt. of halogen (as found out by titration)} \times \text{depression actual} \times 1000.}{\text{depression theoretical} \times \text{mol. wt. of halogen} \times \text{volume of solution}}.$$

The degree of dissociation of the acids is calculated from their freezing points observed and calculated, compared with that for water. These are given as Δ_{actual} and $\Delta_{\text{calc.}}$ against their respective names in the following tables. The following expression gives the degree of dissociation for the acids

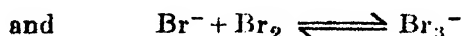
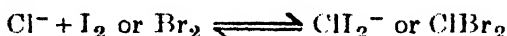
$$\alpha_1 = \frac{\Delta_{\text{actual}}}{\Delta_{\text{calc.}}} - 1.$$

Any change in the degree of dissociation of the acids by the formation of the complexes is neglected. It is further assumed that any complex polyhalogen acid that might be formed is dissociated electrolytically almost to the same extent as the simple halogen acid, and behaves in all respects like the complex polyhalide ion.

Applying the law of mass action, the above equation is obtained for the balanced reactions



or expressed ionically



The heat of formation of the complex polyhalide was calculated according to the well-known formula—

$$\log K_1 - \log K_2 = \frac{Q \text{ (cals)}}{1.985} \times \frac{T_2 - T_1}{T_1 \cdot T_2} \times 0.4343$$

The degree of dissociation of the complex can be calculated from the ratio $\alpha_2 = \frac{\Delta \text{ actual}}{\Delta \text{ calc.}}$ for the corresponding solutions.

Formation and Dissociation of the Compound, HClBr₂.

The reaction between bromine and hydrochloric acid of varying concentrations ($N-N/16$) was studied. For this purpose the hydrochloric acid was shaken at the ordinary temperature with bromine in well stoppered glass bottles until equilibrium was established. 25 c.c. of the bromine solution in hydrochloric acid was measured out from a burette direct to the freezing point tube and the freezing point determined. The supercooling was not allowed to exceed 0.3° , and the freezing was induced by the introduction of a tiny ice crystal. Mixture of ice and salt was used in the cooling bath, the temperature of which was kept about 2.8° below freezing point. Pure potassium iodide was then introduced into the freezing point tube and the amount of iodine found out by titration with $N/2$ -thio-sulphate. The freezing point of the acid alone was previously

determined in the same way. Any volume change that might result from the dissolution of bromine was neglected.

The constancy of the value of the equilibrium constant K , calculated on the assumption that the compound HClBr_2 is formed, justifies the assumption. In this connection it is to be noted that the mean values of K for the different concentrations of the halogen acid appear to vary slightly (Table I). This can be easily explained by the fact that the freezing points of the halogen acids of different concentrations, and hence the temperatures at which the reaction is carried out, are different. Thus the value of K should naturally vary. It is also to be noted that the value of the equilibrium constant K at 30° , as found out by Ray and Sarkar (*loc. cit.*), is 1.412; but at -1.535° it is 1.727. From these it is apparent that the reaction $\text{Cl}^- + \text{Br}_2 \rightleftharpoons \text{ClBr}_2^-$ is exothermic, and it is possible that at low temperatures the compound HClBr_2 might exist in the free state. This assumption is also confirmed by the fact that the heat of reaction, calculated from the mean values of K for the two temperatures, has been found to be positive.

TABLE I*
Formation of HClBr_2 .

	Depression actual.	Depression calc.	Conc. of Br_2 in g. per 25 c.c.	Equi. const. K .	Degree of dissocia- tion α_2
N/HCl	3.655	1.858	0.0
$\text{N}/\text{HCl} + \text{Br}_2$	0.200	0.4874	1.0492	1.874	0.4103
	0.120	0.3107	0.6686	1.836	0.3862
	0.085	0.2259	0.4864	1.852	0.3762
	0.060	0.1542	0.3319	1.708	0.3891
				Mean 1.817	
$\text{N}/2\text{-HCl}$	1.855	0.929	0.0
$\text{N}/2\text{-HCl} + \text{Br}_2$	0.205	0.3531	0.7602	1.714	0.5806
	0.170	0.3004	0.6468	1.780	0.5868
	0.095	0.1732	0.3729	1.840	0.5486
	0.060	0.1033	0.2223	1.708	0.5809
				Mean 1.750	

* The freezing point data are given to the third significant place in decimals, but the results are accurate within $\pm 1\%$. The value of the equilibrium constant is not much affected by the uncertainty.

TABLE I (contd.)
Formation of HClBr_2 .

	Depression actual.	Depression calc.	Conc. of Br_2 in g. per 25 c c.	Equi. const. K.	Degree of dissocia- tion α_2 .
$N/4\text{-HCl}$	0.921	0.4645	0.0
$N/4\text{-HCl} + \text{Br}_2$	0.190	0.2593	0.5581	1.698	0.7330.
	0.170	0.2312	0.4976	1.667	0.7352
	0.140	0.1921	0.4135	1.669	0.7288
	0.042	0.0595	0.1280	1.756	0.7023
				Mean 1.705	
$N/8\text{-HCl}$	0.465	0.2322	0.0
$N/8\text{-HCl} + \text{Br}_2$	0.175	0.2080	0.4478	1.741	0.8412
	0.157	0.1858	0.3998	1.621	0.8450
	0.095	0.1140	0.2456	1.723	0.8333
	0.060	0.0721	0.1542	1.758	0.8324
				Mean 1.699	
$N/13\text{-HCl}$	0.230	0.116	0.0
$N/16\text{-HCl} + \text{Br}_2$	0.127	0.1414	0.3039	1.624	0.8982
	0.100	0.1106	0.2381	1.828	0.9041
	0.070	0.0794	0.1708	1.577	0.8851
				Mean 1.663	

Mean value of $K = 1.726$

Mean temperature = -1.535°

The heat of formation was calculated between the mean value of K at -1.535° (i.e., 1.727), and that of K at 30° (i.e., 1.412) (Ray and Sarker, *loc. cit.*) and was found to be 1044 calories. The heat of formation for ClBr_2 (KClBr_2) as found by Job (*loc. cit.*) is 1000.

Formation and Dissociation of the Compound, HClI_2 .

The reaction between iodine and hydrochloric acid can only be studied in concentrated acid solution. Owing to the sparing solubility of iodine in hydrochloric acid, the reaction could not be studied with acids below the normal strength. In the case of hydrochloric acid of higher concentrations, the freezing point was found to be very low; the freezing point of $2N\text{-HCl}$ is about -7° ; that of $4N\text{-HCl}$ about -15° and so on. At these low temperatures, the composition of the solid separated might not be pure ice, and so

complications might arise. Thus the results with higher strengths of the acid could not be regarded as reliable, and the reaction was, therefore, studied only with the normal hydrochloric acid. The same procedure as in the previous case was adopted, the titration was made with $N/20$ thiosulphate.

The mean value of the equilibrium constant K was found to be 1.836 at -3.771° . The heat of formation was calculated between this value and that of K at 25° , i.e., 1.60 (Ray and Sarker, *loc. cit.*), and was found to be 762 calories. The value for the corresponding ion $\text{ClI}_2/(\text{KClI}_2)$ found by Job (*loc. cit.*) is 695.

TABLE II.

Formation of HClI_2 .

	Depression actual.	Depression calc.	Conc. of I_2 in g. per 25 c.c.	Equi. const. K .	Degree of dissocia- tion α_2
$N\text{-HCl}$	3.655	1.858	0.0
$N\text{-HCl} + \text{I}_2$	0.027	0.0768	0.2517	1.894	0.3516
	0.020	0.0542	0.1842	1.797	0.3690
	0.015	0.0433	0.1471	1.818	0.3464
Mean 1.836					

Formation and Dissociation of the Compound, HBr_3 .

When the reaction was studied with hydrobromic acid and bromine, abnormal results were obtained with normal hydrobromic acid, and with higher concentrations of bromine in semi-normal acid; the freezing points instead of being depressed were found to be elevated. It was thought that this elevation was due to the separation of some solid with ice, whereby the concentration of the acid was diminished. The compound separated can not be bromine hydrate, as can be judged from the results of analysis, given hereafter. The formation of any solid hydrate of hydrobromic acid is, however, excluded, as the experiment was conducted at about 4° , which is considerably above the stability of such hydrates. Normal results were, however, obtained with low concentrations of bromine in hydrobromic acid of lower strengths ($N/2 - N/16$). The equilibrium constants of the reaction are given in Table III.

TABLE III.

Formation of HBr₃.

	Depression actual.	Depression calc.	Conc. of Br ₂ in g. per 25 c.c.	Equi. const. K.	Degree of dissociation α_2
N.HBr	3.511	1.858	0.0
N.HBr + Br ₂	-0.155	0.7649	1.646
	-0.112	0.5955	1.262
	-0.100	0.5358	1.153
	-0.105	0.5148	1.108
N/2.HBr + Br ₂	1.805	0.929	0.0
N/2.HBr + Br ₂	-0.010	0.6690	1.422
	0.0	0.6141	1.322
	0.055	0.3715	0.7982	19.74	0.1480
	0.020	0.1786	0.3845	21.04	0.1119
Mean 20.39					
N/4.HBr	0.920	0.4645	0.0
N/4.HBr + Br ₂	0.075	0.2906	0.6256	21.40	0.2581
	0.037	0.1716	0.3694	20.43	0.2156
Mean 20.91					
N/8.HBr	0.465	0.2322	0.0
N/8.HBr + Br ₂	0.145	0.2874	0.6183	20.36	0.5046
	0.060	0.1531	0.3294	20.91	0.3912
Mean 20.63					
N/16.HBr	0.230	0.116	0.0
N/16.HBr + Br ₂	0.152	0.2463	0.5301	20.97	0.6172
	0.115	0.1779	0.3827	19.28	0.6464
Mean 20.13					
Mean value of K = 20.515					
Mean temperature = -0.945°					

The heat of formation was calculated between this value and that of K at 25°, i.e., 16.2 (Lewis and Randal, *J. Amer. Chem. Soc.*,

1916, 38, 2354), and was found to be 1467 calories. This is of the same order as those found by other investigators as given below.

Berthelot (<i>Compt. Rend.</i> , 1882, 94, 1618)	1290 calories
Lewis and Randal (<i>loc. cit.</i>)	1650
Job (<i>loc. cit.</i>)	2030

Preparation of HBr_3 crystals.—A concentrated solution of bromine in hydrobromic acid (about 1.5 N) was prepared and then allowed to freeze. The solid, separated, was filtered rapidly on the pump through an ice-cold filter and washed with a few drops of ice-cold water free from the adhering liquor. The yellow crystals mixed with ice was transferred quickly to a measuring flask, the solution made up to the mark with cold water. 50 c.c. of this solution was taken and the amount of free bromine estimated by titration with N/100 thiosulphate. Sulphur dioxide was then passed through another 50 c.c. to reduce the bromine to hydrobromic acid. The total bromine was then estimated as silver bromide in presence of nitric acid. The ratio of the weight of free bromine and combined bromine was calculated and found to agree with that for the compound HBr_3 . (Table IV).

TABLE IV.

Composition of Yellow Crystals.

Wt. of combined Br_2 (a)	0.01314g.	0.01793g.	0.01946g.	0.02266g.
Wt. of free Br_2 (b)	0.02797	0.08688	0.04051	0.04797
Ratio b/a	2.128	2.056	2.081	2.117.

The ratio was found to agree closely with that calculated for the compound HBr_3 . (i.e., 2), and hence it is deduced that the compound found is HBr_3 .

Formation of the Compound, HBrI_2 .—Abnormal results were uniformly obtained in the reaction between hydrobromic acid and iodine, the freezing point instead of being depressed was actually found to be raised. The higher the concentration of the halogen, the more was the elevation of the freezing point (Table V). This elevation of the freezing point was believed to be due to the separation of the compound HBrI_2 with ice, whereby the concentration of the halogen acid diminished. With this idea in view, a concentrated solution of iodine in hydrobromic acid (about 1.5N

was prepared and strongly cooled (about -4°). The solid, (orange red crystals mixed with ice) separated, was filtered and made up to a definite volume as in the previous case. 50 c.c. of this solution was measured off, and the free iodine determined with N/100 thiosulphate. Sulphur dioxide was passed through another 50 c.c. to reduce the iodine to hydriodic acid. The total halogen was estimated as silver halides, and the amount of bromine found out by subtracting the amount of iodine previously determined. The ratio between the weights of iodine and bromine was found to agree with that for HBrI_2 (Table VI).

TABLE V.

	Elevation actual.	Depression calc.	Conc. of I_2 in g. per 25c.c.
$\text{N-HBr} + \text{I}_2$	0.032	0.05644	0.1980
	0.020	0.03774	0.1290
	0.022	0.02584	0.08835
	0.015	0.01828	0.06247
	0.002	0.01286	0.04398
$\text{N/2-HBr} + \text{I}_2$	0.012	0.01936	0.06616
	0.007	0.01492	0.0510
	0.0	0.008	0.02735

TABLE VI

Composition of Orange Red Crystals.

	Wt. of I_2 . a	Wt. of $\text{AgBr} + \text{AgI}$.	Wt. of Br_2 . b	Ratio a/b.	a/b for HBrI_2 (calc.)
I.	0.01478 g.	0.03752 g.	0.00433 g.	3.412	
II.	0.02051	0.05227	0.006087	3.370	3.175
III.	0.02505	0.06446	0.007709	3.247	
IV.	0.03007	0.07706	0.009116	3.298	
				3.331	

Formation of the compound, HI_3 .—Abnormal results were also obtained in the reaction between iodine and hydriodic acid, the freezing point was always found to be raised. The solid (red crystal mixed with ice) was separated and analysed as in the previous case. The ratio between the weights of free iodine and combined iodine was calculated and found to agree with that required for the compound HI_3 (Table VII).

TABLE VII.

Composition of the Red Crystals.

	Wt. of I_2 (free) a.	Wt. of I_2 (combined) b.	Ratio a/b.	a/b for HI_3 (calc.).
I.	0.01877 g.	0.008751 g.	2.144	
II.	0.02218	0.01019	2.176	2.0
III.	0.03523	0.01750	2.013	
			2.111	

Osaka (*Z. Phys. Chem.*, 1901, 38, 743) also observed that a solution of iodine in hydriodic acid raises the freezing point of the latter. This was explained by him on the assumption that the affinity constant of the iodides is greater than that of the tri-iodides, and hence the total concentration of ions and undissociated molecules decreases with the addition of iodine. From this he concluded that Dawson's assumption, that the affinity constants for iodides and tri-iodides have the same value, was wrong. From a consideration of the above results, however, proving the actual separation of HI_3 crystals with ice, it can now be affirmed that Osaka's conclusion is obviously wrong and that of Dawson is right.

It will be noticed from the results of analysis for HBr_3 , HBrI_2 and HI_3 that the ratio between the free and combined halogen is always a little high, which evidently indicates the formation of higher polyhalides in concentrated solutions. This is in agreement with the observation made by Jakowkin (*loc. cit.*).

Summary.

By means of the freezing point depressions, the formation of polyhalides of hydrogen, HClBr_2 , HClI_2 and HBr_3 have been confirmed, and their dissociation constants determined at the freezing

points. From the dissociation constants at the freezing points, and from those at 25° or 30°, determined by Rây and Sarker (*loc. cit.*) their heat of formation have also been calculated. The following table gives the values of the dissociation constants and the heat of formation of the compounds.

	Dissociation constant. (1/K).	Heat of formation.
HClI_2	0.544	762 calories
• HClBr_2	0.578	1044
HBr_3	0.049	1467

These give a comparative idea of their relative stability, which appears to be in good agreement with the general chemical conception that weak ions tend to form more stable complexes.

It has also been possible to separate the compounds HI_3 , HBr_3 and HBrI_2 in the solid state mixed with ice.

I take this opportunity of expressing my best thanks to Prof. P. R. Rây, M.A. of the University College of Science for his kindly suggesting this piece of work to me and for many helpful advices that I have received from him in this connection.

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The Constitution of Marmelosin. Part I.

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In course of a previous investigation (*J. Indian Chem. Soc.*, 1930, **6**, 759) the important medicinal plant *Aegle Marmelos* or the Indian Bel was thoroughly and completely examined from the root to the leaf by the present authors, who isolated from the fruit a colourless crystalline compound which they named "marmelosin" and which is most probably the active principle of the fruit. The present work is mainly devoted to the elucidation of the constitution of the substance.

Marmelosin is present in the fruit and in no other part of the plant. The percentage varies from 0.03 to 0.37 according to locality and cultivation, the small wild varieties of the fruit containing proportionately speaking much less of the material than the large cultivated variety. The drier the climate the smaller also is the yield of marmelosin. Fruits obtained from Bengal and Assam have often been found to contain more than five times as much marmelosin as those obtained from the U.P. and the Panjab, for the same weight of the fruit.

Marmelosin is a colourless crystalline substance with a faint smell reminding that of Bel. It crystallises in fine silky needles from petroleum ether and in large cubical crystals from alcohol. It is insoluble in water, but on boiling with water for a long time it melts to an oily liquid which on cooling again solidifies to somewhat greasy crystals, the substance being partially decomposed by the process. In ordinary saturated steam it is volatile only in traces, imparting to the condensed water its characteristic smell, but in superheated steam (200-210°), it readily volatilises with partial decomposition into anhydromarmelosin. When carefully heated by itself in a dry tube, it melts, partially carbonises, partly sublimes unchanged and is partly converted into the anhydride which condenses in the cooler parts of the tube. When quickly heated it decomposes completely with evolution of black fumes. Exposed to ordinary diffused sunlight marmelosin slowly assumes a yellow colour. In

strong direct sunlight marmelosin is converted into a sticky yellow resin in course of a week. Results of a series of analyses and determinations of the molecular weight by the cryoscopic, ebulliscope and lead salt methods point to a molecular formula $C_{13}H_{12}O_3$. One of the three oxygen atoms is in an alcoholic hydroxy group since marmelosin forms a monoacetyl, monobenzoyl and a monophenylurethane derivative, and also it dehydrates very easily with formation of anhydromarmelosin. It does not give any colour reaction or precipitate with neutral alcoholic ferric chloride, lead acetate or mercuric chloride.

Although marmelosin does not react with hydroxylamine, phenylhydrazine or semicarbazide, and does not reduce Fehling's solution yet it is found to reduce Tollen's reagent somewhat slowly. In its behaviour towards Tollen's reagent, it seems to resemble the $\alpha\beta$ -unsaturated lactones studied by Thiel (*Annalen*, 1901, 319, 155) and also more exhaustively by Jacobs and Hoffmann (*J. Biol. Chem.*, 1926, 67, 333). This view is confirmed by the fact that marmelosin develops an intense yellow colour with alcoholic caustic potash as in the case of the vast majority of $\alpha\beta$ -unsaturated lactones, and does not give any colour reaction with sodium nitroprusside. Thus all the three oxygen atoms of marmelosin are accounted for, one in an alcoholic hydroxy group and two in a lactonic grouping.

Marmelosin is unsaturated. It decolorises bromine water slowly and bromine in chloroform quite readily. By the action of bromine in alcohol or chloroform on marmelosin, a derivative was obtained containing three bromine atoms in the molecule. Volumetric estimation of unsaturation shows the presence of two double bonds in the compound and this anomalous position with regard to the above tribromo derivative can be explained by the assumption that in marmelosin the two unsaturated linkages are in a conjugated system. By the action of bromine, therefore, two atoms of the element are introduced at the extreme ends of the conjugated system and the third atom enters the molecule by substitution. The tetrabromo derivative of marmelosin which was obtained by the action of a large excess of bromine in carbon tetrachloride on marmelosin, could not be made to solidify.

Marmelosin readily adds on hydrogen by reduction with any strong acid reducing agents with formation of the dihydro derivative. The acetyl derivative of marmelosin could also be reduced and the product thus formed was found to be identical with the compound

obtained by simultaneous acetylation and reduction of marmelosin with zinc dust and acetic anhydride.

Marmelosin is optically active, having in alcohol a *dextro* rotation of $[\alpha]_{30}^0 = +36^\circ$. The optical activity and the *dextro* rotation was preserved in all the derivatives of marmelosin that have been prepared upto this time. The substance does not show any mutarotation.

Marmelosin is readily acted upon by concentrated hydrochloric acid, 75 per cent. sulphuric acid, anhydrous zinc chloride and phosphorus pentachloride and also by the action of heat, with elimination of a molecule of water and formation of anhydromarmelosin which is a colourless crystalline substance with a characteristic terpene like smell. In this formation the alcoholic hydroxy group is lost since anhydromarmelosin is no longer acted upon by acetylating or benzoylating agents. Anhydromarmelosin on account of its highly unsaturated nature soon undergoes transformation in the air and even in a sealed tube with formation of a sticky resinous substance.

By the action of fuming nitric acid on marmelosin, a mononitro derivative has been obtained crystallising in yellow needles. Fuming hydrobromic acid under pressure converts marmelosin into the monohydrobromide with simultaneous formation of large quantities of anhydromarmelosin. On fusion with caustic soda or potash, marmelosin adds on three molecules of water with formation of a compound $C_{13}H_{18}O_6$ which appears to be a hydroxy dibasic acid. A 3 per cent. alkaline solution of potassium permanganate readily acts upon marmelosin with formation of the same compound together with traces of succinic acid.

On distillation with zinc dust marmelosin is converted into anhydromarmelosin together with a number of its liquid and gaseous reduction and degradation products which could not be identified.

EXPERIMENTAL.

Isolation of marmelosin.—It has already been shown (Dikshit and Dutt, *loc. cit.*) that the most suitable solvent for the extraction of marmelosin from the dry Bel powder is petroleum ether, which also extracts the oil contained in the seeds of the fruit. The

proportion of marmelosin in the fruit differs within wide limits according to the locality and variety as the following table will show.

TABLE I.

Origin.	Marmelosin (%)
Wild fruit collected from the jungles of eastern and southern U.P. (mean of six samples)	0.07
Cultivated fruit from Allahabad (three samples)	0.25
Wild fruit from the Panjab	0.03
Cultivated fruit from the Panjab (one sample each, Lahore and Delhi)	0.13
Wild fruit from western U. P. (four samples from Etawah)	0.05
Cultivated fruit from Bengal (two samples, Calcutta and Dacca)	0.32 (Cal.) 0.35 (Dac.)
Cultivated fruit from Assam (one sample from Sylhet)	0.37

To determine which particular portion of the fruit contained the largest proportion of marmelosin, a particular well-grown cultivated sample of the fruit collected locally was dissected and the various parts extracted with petroleum ether. The results are shown in Table II.

TABLE II.

Part of the fruit.	Marmelosin (%)
Outer rind	Nil
Outer layer of pulp	0.15
Inner layer of pulp	0.46
Central core with the seeds and gum removed	0.08
Seeds	0.02
Gum	Nil

From the above it will appear that the greatest concentration of marmelosin is in the inner layer of the pulp, which is also incidentally the sweetest and most eaten by people and administered in disease.

For the extraction of marmelosin, the fully grown but unripe (ripe fruit is difficult to handle on account of its slow drying and fermenting propensities) cultivated fruits were broken to pieces, dried in the sun, ground to a fine powder in a mill and extracted with petroleum ether in a large Soxhlet's extraction apparatus.

From the extract, the solvent was distilled off until the volume was reduced to one-tenth of the original bulk and allowed to stand for a day when crude marmelosin crystallised out. This was filtered, washed with a little petroleum ether and pressed on porous plates until free from the adherent oil. It was then crystallised alternately from petroleum ether and alcohol with the addition of animal charcoal a number of times, until it was perfectly colourless and melted sharp at 103° .

Properties.—Marmelosin has a faint smell of Bel and a slight astringent taste. It is slightly soluble in benzene and petroleum ether, moderately soluble in alcohol, chloroform, ethyl acetate, acetone and pyridine and insoluble in water. It does not reduce Fehling's solution but ammoniacal silver nitrate is slowly reduced. It does not give any coloration or precipitate with ferric chloride, lead acetate, calcium chloride or silver nitrate, but on warming with basic lead acetate, a white precipitate of the lead salt is formed. It is insoluble in dilute caustic soda solution (5%), but on heating it slowly dissolves with a brown colour. On acidification of the alkaline solution, a white precipitate of marmelosin comes down at once, and the mother liquor on standing slowly deposits another substance crystallising in brownish white needles melting at 146° and possessing the same molecular formula as marmelosin. On standing in contact with concentrated hydrochloric acid it is slowly reconverted into marmelosin. In all probability it is a compound with different type of lactonisation than marmelosin.

Marmelosin does not contain any methoxy or ethoxy group, as its treatment with the Zeissel's method of estimation of these groups gave negative results.

Physiologically marmelosin is an exceedingly potent drug and taken in doses of 0.05 g. it acts as a laxative and diuretic with a slight lowering of the respiration and a tendency towards sleepiness. In larger doses it acts as a strong depressant for the heart. A detailed physiological examination of the substance is in progress in the King George's Medical College, Lucknow. (Found: C, 72.47, 72.20, 72.02, 71.95; H, 5.64, 5.18, 5.46, 5.70; M.W. (cryoscopic in benzene), 198, 202, 213; (ebulliscopic in alcohol), 208, 212, 213; (lead salt), 216.5. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.5 per cent. M. W., 216).

Acetylmarmelosin, $C_{13}H_{11}O_2 \cdot O \cdot COCH_3$.—Marmelosin (1 g.) was treated with acetic anhydride (5 c.c.) and fused zinc chloride

(2 g.) and the mixture heated under reflux for 15 minutes. On pouring into water a heavy oil separated which gradually solidified on long standing. This was crystallised from dilute alcohol in colourless silky needles melting at 214° . (Found: C, 69.51; H, 5.7. $C_{15}H_{14}O_4$ requires C, 69.76; H, 5.4 per cent.).

Benzoylmarmelosin, $C_{13}H_{11}O_2 \cdot O \cdot COC_6H_5$.—Marmelosin (1 g.) was dissolved in pyridine (30 c.c.) and benzoyl chloride (8 c.c.) gradually added with vigorous shaking. The mixture was then heated on the water-bath for $\frac{1}{2}$ hour and poured into excess of dilute hydrochloric acid, when a voluminous white precipitate was obtained. This was filtered off and digested with dilute sodium carbonate solution in order to remove the benzoic acid formed and the residue crystallised from acetic acid with the addition of animal charcoal in pale brownish white needles, m.p. $119-20^{\circ}$. (Found: C, 74.71; H, 5.8. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0 per cent.).

Marmelosin-phenylurethane, $C_{13}H_{11}O_2 \cdot O \cdot NHCOC_6H_5$.—Marmelosin (1g.) was treated with phenylisocyanate (5 c.c.) and the mixture warmed on the water-bath for 1 hour. On allowing the product to stand at the ordinary temperature for 1 day, the phenylurethane derivative crystallised out which was filtered off and washed with benzene until the smell of phenylisocyanate had completely disappeared. The substance was then recrystallised from alcohol in colourless silky needles, m.p. 245° . (Found: C, 71.41; H, 5.32. $C_{20}H_{17}O_4N$ requires C, 71.64; H, 5.07 per cent.).

Monobromomarmelosin dibromide, $C_{13}H_{11}O_3Br \cdot Br_2$.—Marmelosin (2 g.) dissolved in chloroform (120 c.c.) was treated with excess of bromine (4 c.c.) and the mixture allowed to stand for 4 hours in a dark place. It became quite warm and fumes of hydrogen bromide were given off. The solvent and the excess of bromine were then distilled off from a water-bath when a pasty semi-solid mass was obtained, which on standing over quick lime in a desiccator for nearly a month, solidified to a vitreous yellow mass. This on crystallisation from dilute alcohol with the addition of animal charcoal gave pale yellow microscopic needles, m. p. 82° . (Found: Br, 52.4. $C_{13}H_{11}O_3Br_3$ requires Br, 52.6 per cent.).

The volumetric estimation of unsaturation in marmelosin was carried on as follows—marmelosin (0.3432 g.) was dissolved in carbon tetrachloride (10 c.c.) in a stoppered 250 c.c. measuring flask and N/8-bromine (20 c.c.) in the same solvent added and the mixture allowed to stand in a dark place for 24 hours. The mixture was then

cooled in ice and water (25 c.c.) quickly added and well shaken and then 10 p.c. potassium iodide solution (25 c.c.) with water (75 c.c.) introduced and the whole thoroughly agitated. The iodine thus liberated was titrated against N/10-sodium thio-sulphate. After titration, 2 p.c. potassium iodate (5 c.c.) was added and the titration repeated. Twice this value was deducted from the above titration value and the equivalents of bromine atoms taken up by the marmelosin molecule calculated, which came to 3.94. This means two double bonds in marmelosin.

Nitromarmelosin, $C_{13}H_{11}O_3 \cdot NO_2$.—Fuming nitric acid (30 c.c.) was cooled to 0° in a freezing mixture and marmelosin (2 g.) gradually added with thorough shaking. The mixture was allowed to stand at 0° for about 2 hours and then pieces of ice were added which caused the precipitation of a yellow flocculent substance. This was filtered and crystallised from acetic acid in golden yellow microscopic needles, m.p. 97° . (Found: N, 5.16. $C_{13}H_{11}O_5N$ requires N, 5.4 per cent.).

Dihydromarmelosin, $C_{13}H_{14}O_3$.—Marmelosin (2 g.) was dissolved in hot glacial acetic acid (100 c.c.) and the mixture treated with zinc dust (10 g.) in small quantities at a time. When the metal had nearly dissolved, the mixture was filtered hot into a large volume of cold water and the resultant white precipitate filtered off and crystallised from dilute alcohol in colourless needles, m.p. 238° . Unlike marmelosin this substance does not decolourise bromine water. (Found: C, 71.56; H, 6.62. $C_{13}H_{14}O_3$ requires C, 71.56; H, 6.41 per cent.).

Acetyldihydromarmelosin, $C_{13}H_{13}O_2 \cdot O \cdot COCH_3$.—Marmelosin was simultaneously acetylated and reduced by heating the substance (2 g.) dissolved in hot acetic anhydride (50 c.c.) with slightly moist zinc dust (10 g.) and the acetyldihydro derivative isolated in a similar way to the above. It crystallises from dilute alcohol in colourless microscopic needles, m.p. 176° . The substance is easily soluble in most of the organic solvents but insoluble in water. (Found: C, 69.5; H, 6.37. $C_{15}H_{16}O_4$ requires C, 69.28; H, 6.15 per cent.).

Marmelosin hydrobromide, $C_{13}H_{12}O_2 \cdot HBr$.—Marmelosin (2 g.) dissolved in glacial acetic acid (100 c.c.) was treated with fuming hydrobromic acid (10 c.c.) and the mixture heated under pressure in a tightly corked Florence flask immersed in a boiling water-bath. After 12 hours heating the flask was cooled and carefully opened and the contents poured into excess of cold water. The resultant

voluminous brown precipitate was filtered off and crystallised from dilute acetic acid with the addition of animal charcoal in brownish white microscopic needles, m.p. 156°. The mother liquor from the above on examination was found to contain comparatively large quantities of anhydromarmelosin. (Found: Br, 27.3. $C_{13}H_{13}O_3$ Br requires Br, 26.9 per cent.).

Anhydromarmelosin, $C_{13}H_{10}O_3$.—Finely powdered marmelosin (2 g.) was treated with sulphuric acid (75 p.c., 50 c.c.) and the mixture heated on the water-bath under reflux for 12 hours. On dilution with water a light brown oil separated out which was thoroughly washed with water by decantation and then extracted with ether. After drying with anhydrous calcium chloride the ether was removed by distillation and the residual viscous oil allowed to stand in the vacuum desiccator for a week, when it solidified to a crystalline mass. This was recrystallised from petroleum ether with the addition of animal charcoal in colourless silky needles, m.p. 76°, and possessing a penetrating terpene like odour. The substance is easily soluble in most of the organic solvents, but insoluble in water. Unlike marmelosin it is readily volatile in steam and can also be purified in this way. (Found: C, 78.92; H, 5.8. $C_{13}H_{10}O_2$ requires C, 78.78; H, 5.5 per cent.).

Action of heat on marmelosin.—Marmelosin (2 g.) was heated in a small conical flask fitted with an air condenser and suspended in an air-bath. The temperature of the latter was raised at the rate of one degree per minute. Marmelosin at first melted to a colourless liquid which gradually passed through various shades of yellow and brown to almost black and evolved vapours which condensed on the sides of the condenser in the form of glistening crystals. The latter which melted at 76° was identified to be anhydromarmelosin, while from the black carbonaceous residue a further quantity was recovered by steam distillation. The residue left after this, on extraction with alcohol, yielded small quantities of unchanged marmelosin.

Action of phosphorus pentachloride on marmelosin.—Phosphorus pentachloride readily acted upon marmelosin either in the solid state or in benzene solution with formation of anhydromarmelosin. No chloro derivative of marmelosin could be isolated from the reaction mixture.

Fusion of marmelosin with caustic potash.—Marmelosin (5 g.), solid caustic potash (30 g.) and water (10 c.c.) were fused together

in a nickel crucible and the melt maintained at 140-50° for $\frac{1}{2}$ hour. On cooling it was dissolved in water and acidified with hydrochloric acid. A brown precipitate was obtained which was filtered off, washed with water and crystallised from dilute alcohol in colourless prisms, m.p. 245°. The substance appears to be an aliphatic acid. (Found: C, 57.33; H, 6.71%). Taking it to be dibasic the molecular weight by the lead salt and the silver salt comes to 267.3 and 269.2 respectively. From these data the formula $C_{13}H_{18}O_6$ appears likely.

The aqueous mother liquor from the above precipitate on extraction with large quantities of ether and subsequent evaporation of the solvent yielded another substance crystallising from small quantity of water in colourless prisms, m.p. 98° and which was identified to be oxalic acid.

Oxidation of marmelosin with potassium permanganate.—Marmelosin (5 g.) in dilute caustic soda solution was treated with a 3 p.c. aqueous solution of potassium permanganate at the ordinary temperature until the latter was no longer decolourised. The precipitated manganese dioxide was filtered off and from the filtrate on acidification, the same acid melting at 245°, as described above, was isolated in a similar manner. The mother liquor was found to contain traces of succinic acid.

Zinc dust distillation of marmelosin.—Marmelosin (5 g.) on distillation with zinc dust in the usual manner yielded a viscid yellow oil smelling strongly of anhydromarmelosin, and from which the latter was recovered in minute quantities by steam distillation. The greater part of the oil did not solidify, nor could it be purified to yield any constant analytical data. Qualitative tests indicated it to be a mixture of hydrocarbons. During the distillation gaseous products were also evolved which did not condense even in a freezing mixture, and consisted mostly of aliphatic hydrocarbons as they burnt on ignition with a luminous non-sooty flame. No other important product could be isolated.

One of us (B.B.L.D.) wishes to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship which enabled him to take part in this investigation.

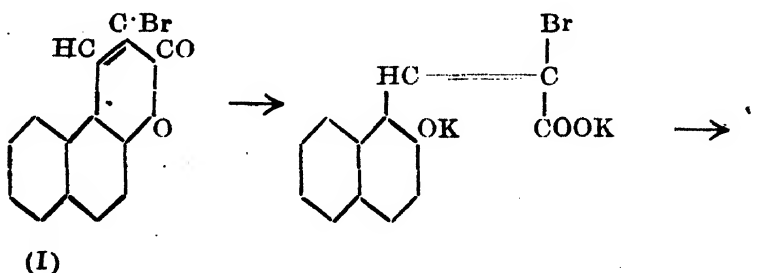
The Stability of Coumarinic Acids Derived from $\beta\alpha$ -1:2-Naphthapyrones.

BY BIMAN BIHARI DEY, RUBUGUNDAY HARI RAMACHANDRA RAO AND
YEGNARAMA SANJARANARAYANAN.

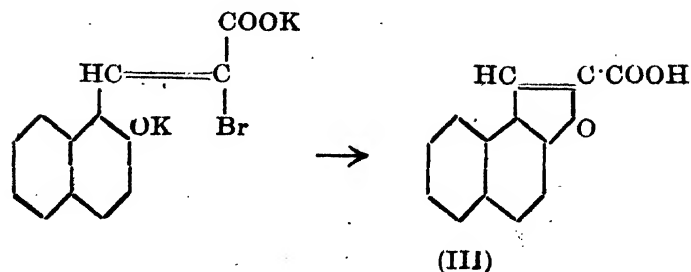
Although coumarinic or *cis-ortho*-hydroxycinnamic acids, as a class, are unstable, and are reconverted into coumarins when a solution of their alkali salts is acidified, there are a few exceptions recorded in literature of moderately stable coumarinic acids such as those derived from 8-nitrocoumarin (Miller and Kinkelin, *Ber.*, 1889, 22, 1706), 3-acetyl-4:5:7-trimethylcoumarin-6:8-dicarboxylic acid diethyl ester (Jordan and Thorpe, *J. Chem. Soc.*, 1915, 107, 387), 6-nitro- $\alpha\beta$ -1:2-naphthapyrone and 6-nitro- $\alpha\beta$ -1:2-naphthapyrone-4-acetic acid (Dey, *J. Chem. Soc.*, 1915, 107, 1606), and a few others. It will be noticed that in all these cases the coumarinic acid is stabilised by the entrance of acidic groups, *e.g.*, nitro or carboxyl, the effect being most marked when the acid radicle is in position-8. Thus the separation of a mixture of 6-nitro- and 8-nitrocoumarins has been made by taking advantage of the superior stability of the coumarinic acid derived from the latter (Dey and Krishnamurthi, *J. Indian Chem. Soc.*, 1927, 4, 197). The entrance of alkyl groups, on the other hand, either in the benzene or in the pyrone rings, is found to produce the opposite effect (*cf.* Hjelt, *Ber.*, 1894, 27, 3832; Fries and Volk, *Annalen*, 1911, 379, 92).

Certain $\beta\alpha$ -1:2-naphthapyrone derivatives, *e.g.*, 4-methyl- $\beta\alpha$ -1:2-naphthapyrone, 3-chloro-4-methyl- $\beta\alpha$ -1:2-naphthapyrone and $\beta\alpha$ -1:2-naphthapyrone-4-acetic acid (Dey, *J. Chem. Soc.*, 1915, 107, 1618) appear, therefore, to be quite exceptional in as much as they provide the only known examples of coumarins yielding stable coumarinic acids notwithstanding the presence of alkyl groups and the absence of any acidic substituents in the ring. The anomaly becomes most striking when the behaviour of these is compared with that of the isomeric $\alpha\beta$ -1:2-naphthapyrones having alkyl substituents in similar positions in the ring. The latter give only unstable *cis*-acids which undergo ring-closure, the moment they are liberated from their alkali salts.

The production of these stable coumarinic acids was considered at first to be characteristic of all $\beta\alpha$ -naphthapyrones, but a study of this reaction with different members of the $\beta\alpha$ -naphthapyrone series has now shown that the stability of the *cis*-acids is apparently connected with the presence of an alkyl group in position-4 in the pyrone ring. This fact was brought into prominence while the action of alkalis on 3-bromo $\beta\alpha$ -1:2-naphthapyrone (I) and 3-chloro-4-methyl- $\beta\alpha$ -1:2-naphthapyrone (II) respectively was being investigated. They exhibited a curious difference: the former reacted normally like other 8-halogen substituted coumarins, and yielded the usual furan derivative (III) with the elimination of alkali bromide, while the latter was converted into the remarkably stable chloro- $\beta\alpha$ -naphthacoumarinic acid (IV) from which no elimination of alkali chloride was possible under the usual conditions.

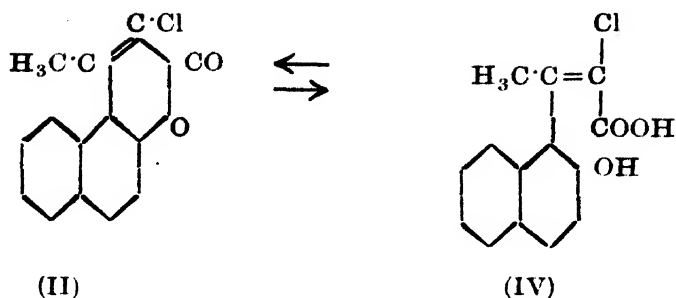


cis- α -Bromo- β -2-hydroxy-1-naphthylacrylic acid (K-salt) (unstable).



trans-Acid,

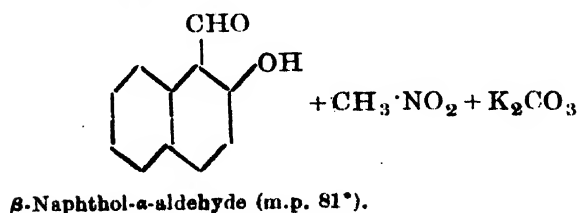
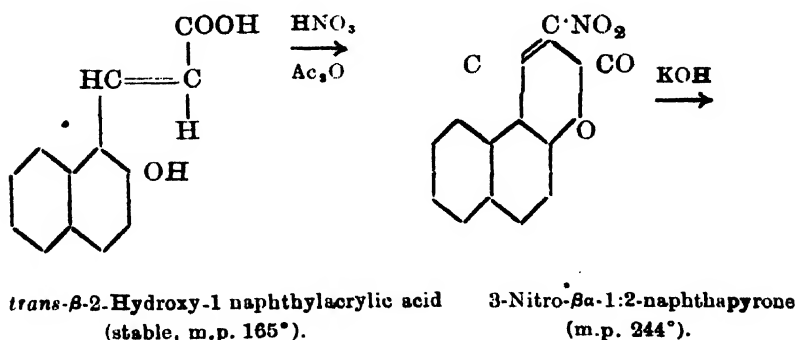
β -Naphthafurancarboxylic acid.



cis-α-Chloro-β-2-hydroxy-1-naphthylcrotonic acid (stable).

The presence of a CH_3 group in position-4 in the pyrone ring, or its absence, must therefore be regarded as the only factor with which this remarkable difference of behaviour with alkalis is associated.

The reaction of 3-nitro- $\beta\alpha$ -1:2-naphthapyrone with alkalis is equally interesting. When the stable *trans*-or β -naphthacoumaric acid is carefully nitrated in acetic anhydride solution, a nitro group enters position-3 with the simultaneous closure of the pyrone ring, and when the nitro derivative is treated with hot alkali, the pyrone ring is completely ruptured and 2-naphthol-1-aldehyde obtained in a quantitative yield. The following equations represent the reactions taking place.



It is clear, therefore, that the entrance of a nitro group makes the pyrone ring unstable.

The stable β -naphthacoumarinic acids have been assigned the *cis*-configurations on the sole evidence of the extraordinary ease with which they are converted into the original coumarins when (a) they are heated to their melting points, (b) they are crystallised from hot solvents like acetic acid, or (c) they are even preserved in a desiccator for several days (*cf.* Dey, *loc. cit.*). It must be noted, however, that hitherto all attempts to convert these stable *cis*-or coumarinic acids into their *trans*-isomers have been unsuccessful, although the other coumarins which give only unstable *cis*-acids have all been converted by the usual methods into the stable *trans*-or coumaric acids. A comparative study of the stabilities of the coumarinic acids derived from a few representative members of the β -1:2-naphthapyrone family has now been made, and the results are summarised in the following table.

Name.	M.p.	<i>cis</i> -Acid.	<i>trans</i> -Acid.
β -1:2-Naphthapyrone	118°	Unstable.	Stable, colourless needles, m.p. 165°.
4-Methyl- β -1:2-naphthapyrone	181°	Stable, soft colourless plates with a pearly lustre, m.p. 146° (decomp.).	Not known.
3-Chloro-4-methyl- β -1:2-naphthapyrone	135°	Stable, colourless mica like plates, m.p. 148° (decomp.).	Not known.
?-Nitro-4-methyl- β -1:2-naphthapyrone	274°	Stable, small yellow prisms, m.p. 271° (decomp.).	Not known.
β -1:2-Naphthapyrone-4-acetic acid	191°	Stable, pale yellow plates, m.p. 174° (decomp.).	Not known.
β -1:2-Naphthapyrone-3-acetic acid	265°	Unstable.	Stable, colourless plates, m.p. 79°.
4-Methyl- β -1:2-naphthapyrone-3-acetic acid	199°	Stable, colourless shining plates, m.p. 154° (decomp.).	Not known.
3-Methyl- β -1:2-naphthapyrone	158°	Unstable.	Stable, colourless plates, m.p. 138°.
3-Bromo- β -1:2-naphthapyrone	165°	Unstable.	Not known. Changes into β -naphthafuran-carboxylic acid, m.p. 192°.
3-Nitro- β -1:2-naphthapyrone	244°	Unstable, decomposes into 2-naphthol-1-aldehyde, m.p. 81°	

The following conclusions may legitimately be drawn from the results tabulated above.

(a) The unsubstituted $\beta\alpha$ -1:2-naphthapyrones or those with a methyl or an acetic acid group in position-3 in the pyrone ring, behave normally and yield only unstable *cis*- or coumarinic acids.

(b) $\beta\alpha$ -1:2-Naphthapyrones having a methyl- or an acetic acid group in position-4, yield stable coumarinic acids, but the latter cannot be transformed by the usual means into the isomeric *trans*- or coumaric acids. The stability of these *cis*-acids is not influenced in any way by the introduction of another atom or group in position-3.

(c) The pyrone ring is rendered unstable by the introduction of negative elements or groups, *e.g.*, Cl, Br, or NO_2 in the 3-position, the latter being removed by boiling alkalis, so long as position-4 is unoccupied.

The work on the influence of substituting groups other than alkyl, *e.g.*, OH, NO_2 , COOH , etc., in position-4, on the stability of *cis*-acids derived from $\beta\alpha$ -1:2-naphthapyrones alone, is in progress.

EXPERIMENTAL.

$\beta\alpha$ -1:2-Naphthapyrone.—This was prepared by modifying the conditions described by Kauffmann (*Ber.*, 1883, 16, 683). The yield was much improved and less tarry matter was associated with the crude product by heating the mixture in a sealed tube at a lower temperature (160°) for 3—4 hours. The product was washed with 50 p.c. methanol, and the residue crystallised twice from boiling absolute alcohol. A maximum yield of 3.8 g. of the pure pyrone (m.p. 118°) was obtained from 5 g. of the naphthol-aldehyde.

trans- β -2-Hydroxy-1 naphthylacrylic acid (β -Naphthacoumaric acid).—On boiling the β -naphthapyrone with 2N-alkali for several hours and acidifying the clear solution, only unchanged coumarin was precipitated. The pyrone (1 g.) boiled with 40 p.c. caustic potash for 5 hours, gave 0.15 g. of the coumaric acid, m.p. 165° (decomp.), the remainder of the coumarin being recovered unchanged. (Found: Eq. wt., 215. $\text{C}_{13}\text{H}_{10}\text{O}_3$ requires Eq. wt., 214).

cis- β -2-Hydroxy-1-naphthylcrotonic acid (4-Methyl- β -naphthacoumarinic acid) (Dey, *J. Chem. Soc.*, 1915, 107, 1630).—The acid crystallised in lustrous plates on acidifying the cooled alkaline

filtrate. It melts sharply at 146° evolving steam and passing over into the original pyrone (m.p. 180°). (Found: Eq. wt., 229.8. $C_{14}H_{12}O_3$ requires Eq. wt., 228).

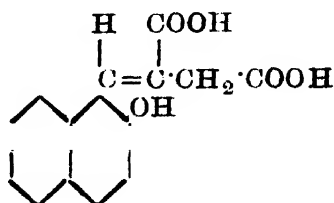
cis- α -Chloro- β -2-hydroxy-1-naphthylcrotonic acid (*β -Chloro-4-methyl- β -naphthacoumarinic acid*) (Dey, *loc. cit.*, 1630).—The acid crystallised in the same way as the preceding acid, m.p. 148° , and passed over into the coumarin (m.p. 135°). (Found: Eq. wt., 266. $C_{14}H_{11}O_3Cl$ requires Eq. wt., 262.5).

?-Nitro-4 methyl- β a-1:2-naphthapyrone.—4-Methyl- β -naphthacoumarinic acid (1 g.) was suspended in acetic anhydride (10 c.c.) and the ice cold mixture treated with the calculated quantity of fuming nitric acid (0.25 c.c.). The solid dissolved immediately and from the clear orange solution, a crystalline solid slowly separated out. The solid was collected after 12 hours, and crystallised twice from hot glacial acetic acid in minute yellow needles sintering at 268° , and melting at 273° . It is insoluble in cold sodium carbonate or alkalis. Analysis showed it to be a pure mononitro derivative. (Found: N, 5.45. $C_{14}H_9O_4N$ requires N, 5.49 per cent.).

cis- β -2-Hydroxy-?-nitro-1-naphthylcrotonic acid.—The clear orange-red solution by boiling the preceding nitro body with 2N-alkali precipitated the acid as a yellow amorphous solid on acidification. It dissolved in cold sodium bicarbonate and was converted at its melting point (271°) into the original pyrone (m.p. 273°). Analysis gave values agreeing with those required for the free acid formed by rupturing the pyrone ring. (Found: N, 5.2. $C_{14}H_{11}O_5N$ requires N, 5.08 per cent.).

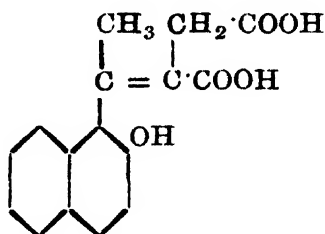
cis- β -2-Hydroxy-1-naphthylglutaconic acid (Dey, *loc. cit.*).—It was prepared from β -naphthapyrone-4 acetic acid as a yellow crystalline powder (m.p. 174°) decomposing at its melting point into the pyrone (m.p. 191°) and water vapour in the manner characteristic of coumarinic acids. The pyrone-acetic acid then loses carbon dioxide and forms ultimately the 4-methyl- β -naphthapyrone (m.p. 180°).

trans- β -2-Hydroxy-1-naphthylitaconic Acid.



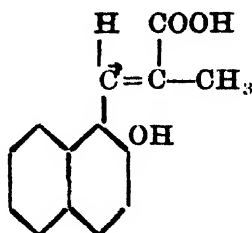
This was prepared from β -naphthapyrone-3 acetic acid (Dey and Sankaranarayan, *J. Indian Chem. Soc.*, 1931, 8, 817) by the method described by Sen and Chakravarti (*J. Indian Chem. Soc.*, 1930, 7, 247). The pyrone (1 g.) is dissolved in 5 p.c. caustic soda (20 c.c.), the solution boiled for 10 minutes, diluted to 60 c. c. and red mercuric oxide (1 g.) added. The mixture was boiled under reflux for 1 hour, filtered and acidified when only an opalescent solution was obtained. This was extracted 4 times with ether (80 c. c.) and the ethereal layer separated and re-extracted with a small quantity of 2 *N*-caustic soda (15 c. c.). On acidifying the alkaline extract, the acid came down in tiny plates, m. p. 75-76°. Crystallisation from the minimum amount of hot glacial acetic acid gave colourless rectangular plates, m. p. 79°. (Found: Eq. wt., 142. $(C_{15}H_{12}O_5)_2$ requires Eq. wt., 136).

cis- $\beta\beta$ -Methyl-2-hydroxy-1-naphthylitaconic Acid.



This was prepared from 4-methyl- β -naphthapyrone-3-acetic acid (Dey and Sankaranarayan, *loc. cit.*) by dissolving in 2*N*-caustic soda at room temperature and acidifying the solution after 1 hour. It crystallised in colourless shining plates, m. p. 154° and changing immediately with separation of water into the pyrone-3 acetic acid (m. p 199°). (Found: Eq. wt., 144. $(C_{16}H_{14}O_5)_2$ requires Eq. wt., 143).

trans- β -2-Hydroxy-1-naphthylmethacrylic Acid.



When 3-methyl- β -naphthapyrone (Bartsch, *Ber.*, 1903, **36**, 1970) was boiled with 40 p.c. caustic soda for 2 hours and the clear solution acidified, only the unchanged material (m.p. 158°) was precipitated. The *trans* or coumaric acid was obtained only through the agency of mercuric oxide by the process described before. It was thrown down from the alkaline filtrate as a white precipitate which crystallised from boiling dilute acetic acid as colourless plates, m. p. 138°. (Found: Eq. wt., 228. $C_{14}H_{12}O_3$ requires Eq. wt., 228).

The *methyl ester*, prepared in the usual way, crystallised from methanol in clusters of colourless plates, m. p. 130°. It is insoluble in alkali carbonate but dissolves in caustic soda with a pale yellow colour.

3-Bromo- β -a-1:2 naphthapyrone.— β -Naphthapyrone (2 g.), dissolved in carbon disulphide (5 c. c.) was treated with a solution of bromine (1.6 g.) in the same solvent (5 c. c.) and the mixture exposed in a silica flask to bright sunlight for 6 hours. The colour darkens on exposure. The solvent was evaporated off at ordinary temperature when a dark red mass presumably containing the dibromide was left as residue. It smelt strongly of bromine and was sparingly soluble in alcohol, but all efforts at getting it in a pure crystalline condition were fruitless. The mass (2.3 g) was suspended in methanol, treated with 2N-caustic soda (5 c. c.) and the mixture heated on a boiling water-bath for $\frac{1}{2}$ hour. The resulting solid crystallised from dilute alcohol in white silky needles, m.p. 165° (decomp.), yield 0.6 g. (Found: Br (by Stepanow's method), 29.26. $C_{13}H_7O_2Br$ requires Br, 29.06 per cent.).

β Naphthafurancarboxylic acid.—The bromopyrone (0.4 g.), dissolved in alcohol (10 c. c.) was treated with 30 p. c. caustic potash (5 c. c.) and warmed on the water-bath. The clear solution very soon deposited crystals of the sparingly soluble potassium salt of the furancarboxylic acid. It dissolved on boiling with excess of water and crystallised again in fine yellow needles on cooling the solution. The free acid (m. p. 192°) was obtained by trituration with hot water containing hydrochloric acid. (Found: Eq. wt., 215.3. $C_{13}H_8O_3$ requires Eq. wt., 212).

3-Nitro- β -a-1:2 naphthapyrone.—Direct nitration of the pyrone generally resulted in a mixture from which it was difficult to isolate the pure mononitro derivative. The latter was obtained by nitrating β -naphthacoumaric acid under precisely the same conditions as those employed in nitrating 4-methyl- β -naphthapyrone. It crystallised

from a large volume of hot acetic acid in orange yellow needles, m. p. 244° . (Found: N, 5.85. $C_{13}H_7O_4N$ requires N, 5.81 per cent.).

The position of the nitro group was revealed by the action of hot alkali on the compound. On boiling the nitro body with 30 p. c. caustic potash for a few minutes and acidifying the clear cold solution, a yellow oil separated which, on distilling in steam, passed over and condensed in the receiver as a pale yellow crystalline solid. A single crystallisation from dilute alcohol gave colourless needles melting at 81° not depressed by admixture with 2-naphthol-1-aldehyde. It was also identified by conversion into the phenylhydrazone.

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Some Acid Constituents of Jute Fibre.

By J. K. CHOWDHURY AND M. N. MITRA.

The presence of acid substances in jute fibre may be surmised from the wellknown fact that in dyeing, jute behaves like a tanned fibre and has direct affinity for basic dyes. This surmise receives further support from the fact that when boiled with 12 per cent. hydrochloric acid, jute fibre evolves considerable amount of carbon dioxide, indicating the presence of acids belonging to the "uronic" group. The present investigations were undertaken with a view to isolate and identify the various acidic substances that might be present in jute and as a result galacturonic, glycuronic and pectic acids have been found present in the fibre.

The separation and isolation of glycuronic and galacturonic acids are particularly difficult when they occur side by side in any substance. Glycuronic acid has been separated by us from the major part of galacturonic acid by taking advantage of the easy oxidisability of the latter by means of air, while galacturonic acid has been separated from glycuronic acid through the barium salt.

Unlike glycuronic acid, galacturonic acid could not be obtained in crystalline form. Both these uronic acids yielded carbon dioxide and furfural when treated with 12 per cent. hydrochloric acid. The carbonic acid and furfural values served as a means for their characterisation. Both reduced Fehling's solution and responded to Mohl's test. On boiling with 2.5 per cent. sulphuric acid, decarboxylation took place and glycuronic acid yielded xylose while galacturonic acid yielded arabinose. Bromine water oxidised the former to saccharic acid and the latter to mucic acid. Both formed cinchonine salt which served as a means for their identification.

Crude pectin extracted from jute with 5 per cent. ammonium oxalate was purified and then converted into free pectic acid by the method of Candlin and Schryver (*Proc. Roy. Soc.*, 1928, **B**, 103, 367).

Unlike the pectic acid from onion and citrus as obtained by the above workers, the pectic acid from jute was found to give colloidal solution with water and had, therefore, to be precipitated from its ammonium salt by alcohol acidulated with concentrated hydrochloric acid. The yield was 2.18 per cent. (calculated on delignified jute).

The pectic acid, thus obtained, was a very light, absolutely white amorphous powder and gave insoluble salts of heavy metals. It became greyish black at 195-97° and melted with decomposition at 233-95°. It was found insoluble in almost all the usual organic solvents. When heated with acid and alkali decarboxylation and hydrolysis took place. This was evidently the reason that it could not be detected in the ammonium extract from which the uronic acids were isolated. On heating with dilute acid (1 N-sulphuric acid), hydrolysis without any decarboxylation took place but when boiled with 7.5 per cent. sulphuric acid, hydrolysis and decarboxylation proceeded simultaneously and 15.81 per cent. galactose was found in the products of hydrolysis.

Special mention may here be made of the furfural value of the uronic acids. Nanji, Paton and Ling (*J. Soc. Chem. Ind.*, 1925., **44**, 253r) mention 33 per cent. as the furfural value of these uronic acids while Norman (*Biochem. J.*, 1929, **23**, 1353) gives 16.66 per cent. as the furfural value of uronic anhydride. None of the investigators have, however, furnished any experimental data in support of these figures. The furfural value of glycuronic acid has been determined by us and found to be 21.84 per cent. This figure is in fair agreement with that of galacturonic acid (19.96 p.c.) determined by Ehrlich and Schubert (*Ber.*, 1929, **62**, 2012). It is evidently incorrect to estimate the pentoses in plant products from the furfural value alone, a part of which must be attributed to the uronic acids. In the light of the present determination of the furfural value of uronic acids as 21.84 per cent., it will be seen that about 1/5th of the total furfural yield of jute fibre must be attributed to the presence of these acids and only the rest to pentosans.

EXPERIMENTAL.

Delignification of jute fibre was carried out by chlorine peroxide gas in large soda-lime towers with ground glass joints. The fibre was, however, previously boiled with 0.5 per cent. caustic soda solution

for 1 hour in order to facilitate the removal of lignin. The analytical data of the raw and delignified jute are given below.

	Raw jute. (%).	Delignified jute (%).
Lignin	12.74	Nil
α -cellulose		66.82
Ash	0.605	
Fat & resin	0.585	Nil
Furfural	11.503	10.894 (calc. on raw jute)
Uronic acids	10.824	10.924 („ „)

Extraction with ammonium hydroxide.—The delignified fibre was extracted with 17 per cent. ammonium hydroxide for 6 hours at a stretch at 45°. The excess of ammonia was driven off from the brown extract at a low temperature. It was found that about three extractions were necessary to make the fibre free from uronic carbon dioxide.

Isolation of glycuronic acid.—A portion of the extract was treated with basic lead acetate when a yellowish precipitate was obtained which was washed free from lead. This was suspended in water and decomposed with sulphuretted hydrogen. Considerable difficulties were experienced in removing the precipitate of lead sulphide owing to its colloidal nature. Precipitation was, however, facilitated by the addition of a little alcohol to the filtrate which had been previously freed from the sulphide as far as possible. The filtrate was decolourised with animal charcoal and concentrated under reduced pressure (15 mm.), a slow current of air being passed through a capillary during evaporation. After a time, white precipitates began to separate out and the syrup was poured in excess of alcohol when a white precipitate was thrown down. It was filtered, washed with alcohol and dried. A part of this substance was found soluble in cold water giving an opalescent solution while the residue, crystallised from hot water, yielded crystals of mucic acid. The opalescence of the solution could be removed with a few drops of acetic acid. It was concentrated under reduced pressure and poured to excess of alcohol. The precipitate was further purified by repeated solution and precipitation and was found to have properties similar to those of glycogen. The alcoholic filtrate,

after precipitation of mucic acid and glycogen, was concentrated in vacuum and left in a vacuum desiccator over sulphuric acid for 2—3 days, when white crystalline needles of glycuronic acid were obtained.

The following tests served to identify and characterise the above mentioned products.

Glycuronic acid melted at 159-61°. The cinchonine salt was prepared by adding a concentrated solution of cinchonine in 96 per cent. alcohol to a 2 per cent. alcoholic solution of glycuronic acid. Crystals were obtained on concentration and standing overnight and were recrystallised from alcohol, m.p. 199-200°. Glycuronic acid yielded 21.84 per cent. furfural as determined by the phloroglucide method. Nitrogen found in the cinchonine salt was 6.03 per cent. (theoretical, 5.74 per cent.). The acid reduced Fehling's solution, turned yellow with caustic soda and responded to the Mohl's test with α -naphthol. Decarboxylation of the acid was effected as follows:

The acid (about 1g.) was boiled with sulphuric acid (130 c.c., 2.5 p. c.) for 3 hours under reflux. The excess of sulphuric acid was removed with powdered barium carbonate and the filtrate was concentrated to a syrup in vacuum. The presence of xylose in the syrup was established by Tollens' Orcinol test and by means of Bertrand's reagent.

Mucic acid as obtained above melted at 214° and the silver salt gave Ag, 6.03 per cent. The tetraacetyl derivative melted at 262-63°.

Glycogen, a white amorphous powder formed an opalescent solution in water, the opalescence being removable by a few drops of acetic acid. Iodine gave a reddish brown coloration which disappeared on heating and reappeared on cooling. It formed insoluble precipitate with basic lead acetate and turned slightly yellow on prolonged exposure to air. Hydrolysis with dilute hydrochloric acid yielded glucose, which was identified by Barfoed's and Nylander's reagents.

Isolation of galacturonic acid.—The delignified fibre was extracted with ammonium hydroxide (5 per cent.) under the same conditions as described before and the extract was freed from ammonia at a low temperature (45°). On the addition of barium hydroxide, the barium salt of glycuronic acid separated out and was washed free from baryta and then decomposed with sulphuric acid, the excess being removed with powdered barium carbonate. The filtrate was

concentrated under reduced pressure. On pouring the resulting syrup in alcohol, a small quantity of mucic acid separated as before while the alcoholic filtrate yielded traces of glycuronic acid.

The mother liquor after separation of barium glycuronate was freed from excess of baryta with carbonic acid gas, was concentrated under reduced pressure and poured in excess of alcohol when the pale yellow precipitate of barium galacturonate separated out. It was decomposed with sulphuric acid, excess of which was removed with barium carbonate and the filtrate was concentrated in vacuum.

The syrup thus obtained reduced Fehling's solution. The cinchonine salt was prepared by treating the barium salt with cinchonine sulphate, the filtrate being concentrated in vacuum and allowed to crystallise. The cinchonine salt was finally obtained in the form of fine white needles after recrystallisation from alcohol, m.p. 155-58°. Nitrogen found in the cinchonine salt was 5.97 per cent. (theoretical, 5.74 per cent.). Decarboxylation of the acid was carried out in the same way as that of glycuronic acid and arabinose was detected in the products of hydrolysis by Tollen's Orcinol test and was confirmed by means of the *p*-bromophenylhydrazone, m.p. 152°.

Isolation of pectic acid.—Delignified jute was extracted with 0.5 per cent. ammonium oxalate at 85-90° until the residual fibre was free from uronic carbon dioxide. The pale yellow extract was concentrated to a small volume and poured in excess of alcohol when a pale yellow gelatinous precipitate slowly separated out. After standing for 24 hours, it was filtered and washed with graded strengths of alcohol and finally with ether. By repeated solution in water and precipitation with alcohol, it was obtained as an almost white gel. To a solution of this pectin in water, an equal volume of saturated lime water was added and the mixture was allowed to stand overnight. The white gel of calcium pectate was treated with a warm solution of ammonium oxalate (2 p. c.), the precipitate of calcium oxalate being filtered off. The clear solution of ammonium pectate was then treated with a large excess of alcohol acidified with concentrated hydrochloric acid and allowed to stand for 24 hours. The white gel of pectic acid thus obtained was washed repeatedly with graded strengths of alcohol, then with ether and finally dried in vacuum. The yield was approximately 2.2 per cent. calculated on delignified fibre. Analysis of this pectic acid yielded ash, 0.066; furfural, 28.1; uronic CO₂, 17.45 and Ag (silver salt), 28.4 per cent.

It may be noted that the above uronic carbon dioxide is equivalent to 69·8 per cent. uronic acid and 98·77 per cent. pectic acid (Nanji, Paton and Ling, *loc. cit.*).

Hydrolysis of pectic acid.—The substance (about 7·5 g.) was treated with 1N- H_2SO_4 (300 c.c.) under reflux for 3 hours at 125-80°. The excess of sulphuric acid was removed with barium carbonate and the filtrate, concentrated to a syrup, was poured in 20 per cent. alcohol. The precipitate thus separated was found to be barium galacturonate, while arabinose and galactose were found in the alcoholic filtrate.

Hydrolysis was next conducted with 2·5 per cent. H_2SO_4 in the manner described above. In this case only arabinose and galactose were found in the products of hydrolysis, galacturonic acid being evidently decarboxylated in the course of hydrolysis. 15·81 per cent. galactose was found in the pectic acid as estimated by the mucic acid method. It is evident that for the identification and estimation of galactose by oxidation to mucic acid, all traces of galacturonic acid must be removed. This was effected by taking advantage of the complete insolubility of the barium salt in 80 per cent. alcohol.

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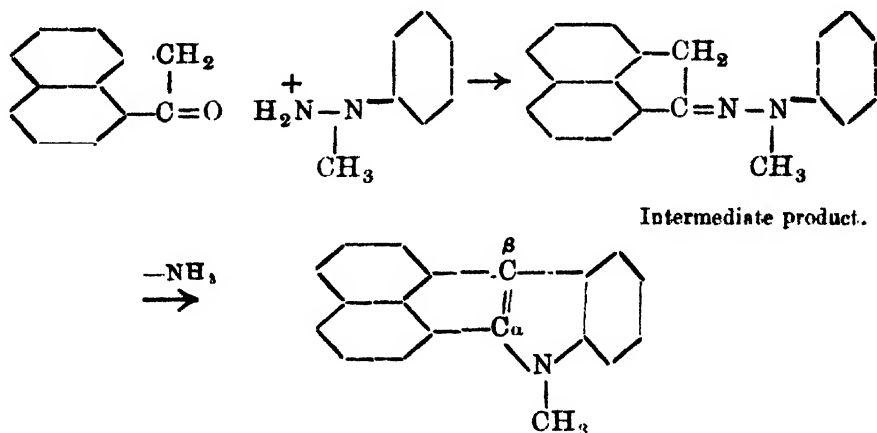
Studies in Acenaphthenone. Part II.

Indole and Acridine Derivatives.

BY ANUKUL CHANDRA SIRCAR AND M. D. RAJA GOPALAN.

In the first paper in this series (*J. Indian Chem. Soc.*, 1932, 9, 108) the preparation of pyrilium derivatives from acenaphthenone has been described. The present paper deals with the preparation and properties of indole and acridine derivatives from acenaphthenone.

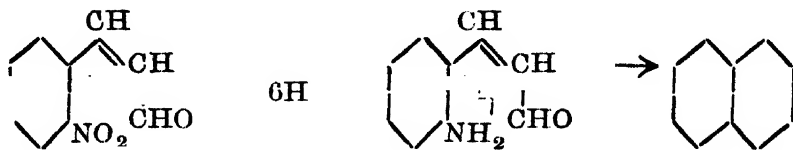
The $\text{-CH}_2\text{CO-}$ group in acenaphthenone has now been utilised for the preparation of indole derivatives by following the procedure indicated by Robinson and Thornley (*J. Chem. Soc.*, 1926, 129, 3145). Acenaphthindole and N-methyl- $\alpha\beta$ -acenaphthindole have been prepared by condensing phenylhydrazine and unsymmetrical methylphenylhydrazine respectively with acenaphthenone.



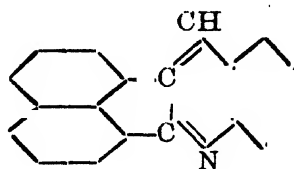
N-Methyl $\alpha\beta$ -acenaphthindole.

The condensation of aromatic *o*-aminoaldehydes with substances containing the group $\text{-CH}_2\text{CO-}$ to quinolines by means of dilute sodium hydroxide constitutes one of the important methods for the synthesis of such bodies (Friedlander, *Ber.*, 1882, 15, 2578; 1883, 16,

1883; 1892, **25**, 1752). Baeyer and Drewson (*Ber.*, 1883, **16**, 2207) instead of using *o*-aminoaldehydes obtained quinolines by the reduction under suitable conditions of the corresponding nitro derivatives.



By following the method of Friedlander (*loc. cit.*), pheno- α 3-acenaphthacridine (I) has now been prepared by the condensation of



(I)

o-aminobenzaldehyde with acenaphthenone. In an attempt to prepare the same compound by the reduction of the condensation product of *o*-nitrobenzaldehyde and acenaphthenone (*cf.* Baeyer and Drewson, *loc. cit.*) the desired product was obtained only in extremely poor yield. The major portion was converted into a red substance, and it appears that the reduction had gone one stage further and the corresponding dihydro derivative had been formed.

EXPERIMENTAL.

Acenaphthindole.—Acenaphthenone (1 g.) and phenylhydrazine (0.65 g.) were dissolved in glacial acetic acid (10 c.c.) and the mixture refluxed on the water-bath for about 2-3 hours. After an hour the solution was found to change colour from pale yellow to deep yellow and then to orange red and gradually fine golden yellow shining plates began to separate. At the end of 3 hours it was found

that a large quantity of yellow plates had deposited. The solution was then diluted with 2—3 c.c. of water and again heated on a water-bath for about 1 hour when more crystals collected. These were filtered and purified by recrystallisation from dilute alcohol in which it is fairly soluble. It forms beautiful golden yellow shining plates, m.p. 235°. It is highly soluble in benzene, chloroform, ether, etc. It gives a blue coloration with concentrated sulphuric acid, and is reprecipitated on dilution. Alcoholic hydrochloric acid can also effect the elimination of ammonia and consequent ring closure. (Found: N, 6.12. $C_{18}H_{11}N$ requires N, 5.8 per cent.).

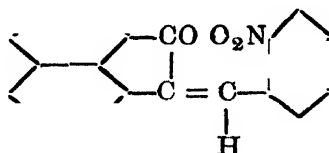
•*N-Methyl- $\alpha\beta$ -acenaphthindole*.—Acenaphthenone (1 g.) and unsymmetrical methylphenylhydrazine (0.8 g.) were dissolved in acetic acid (10 c.c.) and refluxed on a boiling water-bath for 3-4 hours. At the end of about an hour the colour of the solution began to change from orange to deep red and on the heating being continued for some more time, a little of a scarlet red crystalline precipitate began to separate. A little more acetic acid (3 c.c.) was added and the refluxing continued for another 3 hours by which time sufficient quantity of crystals had deposited. These were filtered and recrystallised from boiling acetic acid by the addition of hot water. On cooling, beautiful scarlet-red plates separated, m.p. 204°. It is fairly soluble in alcohol or acetic acid and very soluble in chloroform or benzene. It dissolves in concentrated sulphuric acid imparting to it a dirty green colour. (Found: N, 5.84. $C_{19}H_{13}N$ requires N, 5.49 per cent.).

Pheno- $\alpha\beta$ -acenaphthacridine.—Acenaphthenone (0.7 g.) and *o*-aminobenzaldehyde (0.5 g.) (prepared by Friedlander's method, *loc. cit.*) were dissolved in the minimum quantity of absolute alcohol and to the cold solution a few drops of 10 per cent. alcoholic potash were added. The sides of the vessel on being scratched, golden yellow plates separated. After keeping the reaction mixture for an hour in a cool place, the crystals were filtered and washed with 40 per cent. alcohol. It was purified by dissolving in hot alcohol and to the solution hot water was added slowly when, at a particular dilution, clustres of shining golden yellow plates separated all on a sudden. The crystals were filtered, washed and dried, m.p. 181°. It is soluble in benzene, chloroform or acetic acid, etc. It gives a straw yellow colour with concentrated sulphuric acid from which it is not reprecipitated on dilution. The substance is soluble in hot concentrated hydrochloric acid from which yellow silky needles of

the hydrochloride separate on cooling. (Found: N, 5.93. $C_{19}H_{11}N$ requires N, 5.53 per cent.).

Attempts to Prepare Pheno- $\alpha\beta$ -acenaphthacridine by the Reduction of o-Nitrobenzilideneacenaphthenone.

o-Nitrobenzilideneacenaphthenone.



Equimolecular quantities of acenaphthenone and o-nitrobenzaldehyde were dissolved in the smallest quantity of alcohol and a few drops of 10 per cent. alcoholic potash added. The solid product that separated after some time was filtered, washed with 40 per cent. alcohol, and dissolved in boiling alcohol followed by the addition of animal charcoal and filtered hot. The filtrate, on dilution with a few drops of water deposited on cooling deep yellow shining needles, m.p. 157° . It is highly soluble in benzene or chloroform. It dissolves in concentrated sulphuric acid with a reddish violet colour. (Found: N, 4.73. $C_{19}H_{11}O_3N$ requires N, 4.65 per cent.).

Reduction of o-nitrobenzilideneacenaphthenone.—o-Nitrobenzilideneacenaphthenone (0.5 g.) was dissolved in hot absolute alcohol (20.25 c.c.). When the substance had all dissolved about 1 c.c. of fuming hydrochloric acid was added and 0.3 g. of iron dust (reduced by hydrogen) was then introduced in small quantities at a time. Immediately a pinch of iron was added vigorous action ensued and the solution turned red. After the reaction had ceased and the solution was boiling for 10 minutes, another small quantity of iron was added. After some time a red precipitate began to appear and when all the iron had been added the mixture was kept boiling for another $\frac{1}{2}$ hour. The whole operation took about 2 hours. The precipitate was filtered hot and washed first with water and then repeatedly extracted with concentrated hydrochloric acid by boiling. The hydrochloric acid extract on cooling separated some fine silky needles identified to be the hydrochloride of pheno- $\alpha\beta$ -acenaphthacridine. But the yield was very poor,

The red precipitate left after extraction with hydrochloric acid was dissolved in acetone and filtered from any unchanged iron or iron oxide. On addition of hot water to the acetone solution a brownish-red amorphous precipitate was obtained. It could not be crystallised from any solvent. It is sparingly soluble in chloroform or alcohol. It dissolves in concentrated sulphuric acid imparting to it a violet coloration. Like the dihydroacridines it is insoluble in hydrochloric acid, *i.e.*, has no basic properties. It decomposes between 236-40°. From its properties it is definite that the substance is not pheno- $\alpha\beta$ -acenaphthacridine. (Found: N, 5.58. The acridine requires N, 5.53 and its dihydro derivative requires N, 5.49 per cent.).

When silver nitrate was added to an alcoholic solution of the above reduction product (*cf.* Graebe and Caro, *Annalen*, 1871, 158, 278) the red colour disappeared and a pale yellow solution resulted. On filtering the precipitated silver and diluting the solution, a yellow substance was obtained which melted between 160-70°, though not sharply. The yield being poor it could not be further investigated. This substance might be the desired oxidation product, *viz.*, pheno- $\alpha\beta$ -acenaphthacridine in a very impure form. But in the absence of further proof no definite constitution can be assigned to the red reduction product.

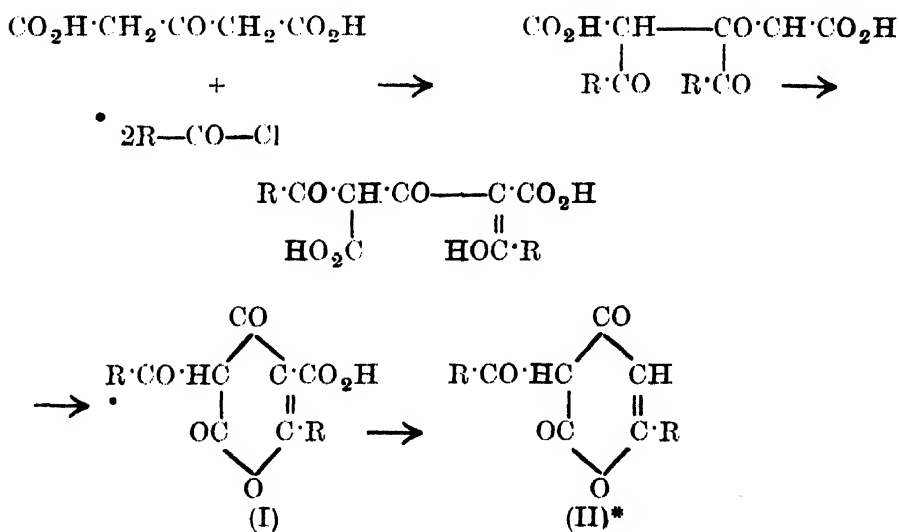
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Synthesis of 2:6-Diethyl-4-pyrone and of 2:6-Di-*n*-propyl-4-pyrone.

By S. S. DESHAPANDE.

Pechmann and Neger (*Annalen*, 1893, **273**, 186) have described the preparation of dehydraacetic acid and dehydrapropionyl acetic acid (II, R=CH₃ or C₂H₅) through dehydraacetocarboxylic acid and dehydrapropionyl acetocarboxylic acid respectively (I) by the action of corresponding acid chloride or anhydride on acetone dicarboxylic acid.

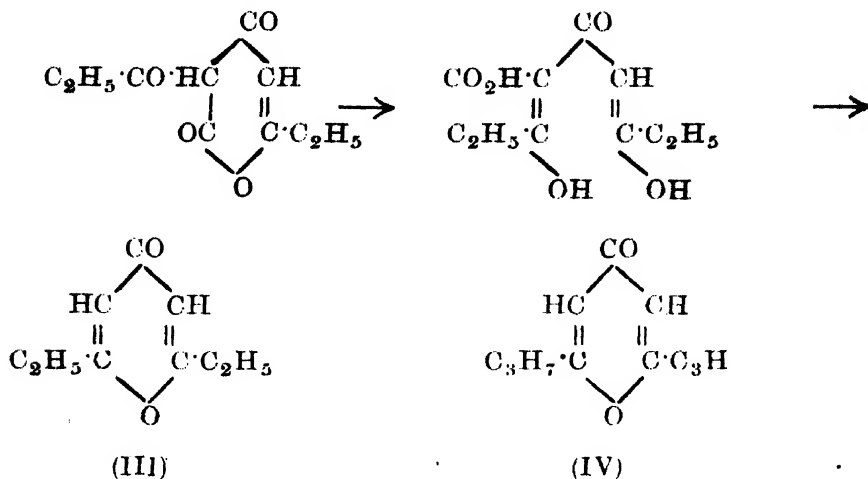


In the present paper this reaction has been extended to the preparation of the corresponding butyryl derivatives by using *n*-butyric anhydride or *n* butyryl chloride (R=C₃H₇).

Further 2:6-diethyl-4-pyrone (III) which from literature does not appear to have been prepared from Pechmann and Neger's dehydra-

* Formula of Feist which has received confirmation in the hands of Rassweiler and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2758).

propionyl acetic acid has now been successfully prepared by boiling the latter with fuming hydrochloric acid.



(cf. preparations of corresponding dimethyl- and diphenylpyrones, Collie, *J. Chem. Soc.*, 1891, **59**, 617; Feist, *Ber.*, 1890, **23**, 3726.)

2:6-Di-*n*-propyl-4-pyrone (IV) has similarly been synthesised from dehydrat-*n*-butyryl acetic acid.

The pyrones (III) and (IV) behave like dimethyl derivative in being weak monoacid bases, and in the inactivity of their carbonyl group. The pyridones corresponding to them have also been obtained. In general 2:6-disubstituted-4-pyrones change by fission of ring into 1:3:5-triketones, *e.g.*, dimethylpyrone changes into diacetylacetone (Feist, *Annalen*, 1890, **257**, 276) and phenylmethylpyrone into benzoylacetylacetone (Ruhemann, *J. Chem. Soc.*, 1908, **93**, 1283), although attempts to prepare dibenzoylacetylacetone from diphenylpyrone have failed (Feist, *Ber.*, *loc. cit.*; Ruhemann, *loc. cit.*). The pyrones (III) and (IV) have yielded the corresponding 1:3:5-triketones; but these and the velocity of transformation of such triketones back into the corresponding pyrones as affected by substituents will be the subjects for future communications.

EXPERIMENTAL.

Dehydrapropionyl acetocarboxylic acid, (I).—Crude acetone dicarboxylic acid (180 g.) was added in instalments and under constant stirring to propionic anhydride (500 g.) kept cool by ice-water. The temperature during addition was not allowed to rise above 10° and

the process was complete in $\frac{1}{2}$ hour when most of the acid was dissolved. The mass was then heated on a water-bath for $\frac{1}{2}$ hour and on cooling poured into water. The precipitated acid after filtration and drying weighed 170 g. Pechmann and Neger (*loc. cit.*) do not mention the yield. It crystallised from dilute alcohol, m.p. 114-15°.

The *monopotassium salt* of the acid was prepared by dissolving the acid in excess of aqueous caustic potash and then making strongly acid by adding acetic acid when the salt precipitated.

Dehydropropionyl acetic acid, (II).—The monopotassium salt of the acid (I) was shaken with sufficient hot water in a flask fitted with water condenser and kept gently boiling for 40 minutes. On cooling and acidifying with acetic acid dehydropropionyl acetic acid was precipitated which was filtered at the pump. 140 G. of dehydropropionyl acetocarboxylic acid gave 92 g. of dehydropropionyl acetic acid, yield 80 p.c. Pechmann and Neger's method gave a poor yield. The acid crystallised from dilute alcohol, m.p. 72°.

2:6-Diethyl-4 pyrone, (III).—A mixture of dehydropropionyl acetic acid (30 g.) and hydrochloric acid (d 1.19, 200 c.c.) was kept gently boiling for 4 hours. On cooling, the liquid was filtered and the bulk of the hydrochloric acid removed by distillation under reduced pressure. The residual liquid was neutralised with cold caustic soda and extracted many times with ether. On drying and removing the solvent, a thin liquid remained which was distilled under reduced pressure when most of it passed between 136-38°/8 mm. On redistillation this boiled at 126°/7 mm. (Found: C, 71.3; H, 7.6. $C_9H_{12}O_2$ requires C, 71.0; H, 7.8 per cent.).

The pyrone is a thin liquid which freezes on cooling. The solid melts at 10°. It readily dissolves in cold water and gives no coloration with ferric chloride. It does not react with phenylhydrazine, nitrophenylhydrazine or semicarbazide.

The *hydrochloride* was prepared in the usual way. It is an extremely hygroscopic solid and can be crystallised from an excess of absolute ether from which it separates in thick prisms, m.p. 77°-78°. (Found: HCl, 19.2. $C_9H_{12}O_2$, HCl requires HCl, 19.3 per cent.).

The *chloroplatinate* is a crystalline solid, m. p. 188° (decomp.). [Found: Pt, 27.4. $(C_9H_{12}O_2)_2$, H_2PtCl_6 requires Pt, 27.3 per cent.].

The *picrate* crystallised from hot water in long yellow needles, m. p. 110°. [Found: Picric acid (by titration), 60.1. $C_9H_{12}O_2$, $C_6H_2(OH)(NO_2)_3$ requires picric acid, 60.1 per cent.].

The pyrone, like dimethylpyrone, gives with mercuric chloride a characteristic crystalline compound, crystallising from water in needles, m. p. 72° (decomp.). (Found: Hg, 47.1. $C_9H_{12}O_2$, $HgCl_2$ requires Hg, 47.5 per cent.).

2:6-Diethyl-4-pyridone.—A solution of the pyrone (3 g.) in strong ammonia (10 c.c.) was heated in a sealed tube at 180° for 4 hours. The contents were evaporated on a water-bath almost to dryness. The crude pyridone was found difficult to crystallise from any solvent. It was purified by crystallising twice from water in which it easily dissolves and from which on standing for some days it separates in thick plates, m. p. $65-66^{\circ}$. (Found: C, 63.9; H, 8.7; N, 8.6. $C_9H_{13}ON$, H_2O requires C, 63.9; H, 8.9; N, 8.3 per cent.).

The hydrochloride melts at $76-78^{\circ}$. (Found: HCl, 17.7. $C_9H_{13}ON$, HCl, H_2O requires HCl, 17.7 per cent.).

The chloroplatinate of the pyridone was prepared as usual and crystallised from dilute hydrochloric acid, m. p. 203° (decomp.). [Found: Pt, 27.3. $(C_9H_{13}ON)_2 \cdot H_2PtCl_6$ requires Pt, 27.3 per cent.].

Dehydro-n-butyryl acetocarboxylic acid, (I, $R=C_3H_7$).—This was prepared from acetone dicarboxylic acid and *n*-butyric anhydride or *n*-butyryl chloride. The product obtained from butyryl chloride was purer and gave better yield than with butyric anhydride. *n*-Butyryl chloride (100 g.) was mixed with strong sulphuric acid (1.5 c.c.) and crude acetone dicarboxylic acid (30 g.) was gradually added to the liquid at room temperature. There was a vigorous evolution of hydrochloric acid gas. After all the acid was added and the vigour of the reaction subsided, the semi-solid mass was gradually heated on a water-bath. In $\frac{1}{2}$ hour the evolution of hydrochloric acid ceased and a clear red liquid was formed. On cooling this was poured on crushed ice and the precipitated acid filtered at the pump. The filtrate contained some thick red oil which after separation from the main bulk and rubbing with water gave a further crop of the acid. The acid crystallised from alcohol in thin light plates, m. p. 80° , yield 16 g. (Found: C, 58.0; H, 5.9. $C_{13}H_{16}O_6$ requires C, 58.2; H, 5.9 per cent.).

The monopotassium salt of the acid crystallised from hot water in long needles, m. p. 164° . (Found: K, 12.1. $C_{13}H_{15}O_6K$ requires K, 12.6 per cent.).

Dehydrabutyryl acetic acid, (II, $R=C_3H_7$).—When the monopotassium salt described above was refluxed with water for 45 minutes and the product made acid with acetic acid, dehydrabutyryl

acetic acid separated as an oil. This was extracted with ether, dried and the solvent removed. The thick liquid which remained was distilled under reduced pressure when practically the whole passed between $140-44^{\circ}/4\text{mm.}$ and was pure enough for analysis. 14G. of crude dehydrabutyryl acetocarboxylic acid gave 8 g. of pure dehydrabutyryl acetic acid. (Found: C, 64.3; H, 7.0. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires C, 64.3; H, 7.1 per cent.).

Dehydrabutyryl acetic acid is a liquid which solidifies on cooling, melting at 16° . The acid is sparingly soluble in water and can be titrated against caustic soda with phenolphthalein as indicator. (Found: M. W. (monobasic), 223. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires M. W., 224.).

2:6-Di-n-propyl-4-pyrone, (IV).—Dehydrabutyryl acetic acid was refluxed with 10 volumes of hydrochloric acid ($d\ 1.19$) for 24 hours. On cooling a small quantity of the undissolved oil which remained was separated and the clear liquid was treated as in the preparation of diethylpyrone. The resulting liquid was distilled under reduced pressure when most of it passed between $140-42^{\circ}/6\text{mm.}$ This on redistillation boiled at $136^{\circ}/5\text{mm.}$ (Found: C, 72.9; H, 8.4. $\text{C}_{11}\text{H}_{16}\text{O}_2$ requires C, 73.3; H, 8.8 per cent.).

It is an oily liquid which does not freeze even at the temperature of freezing mixture. It is sparingly soluble in hot water. The hydrochloride could not be prepared but it gave a picrate which crystallised from dilute alcohol, m. p. 61° . [Found: Picric acid, 55.9. $\text{C}_{11}\text{H}_{16}\text{O}_2 \cdot \text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$ requires picric acid, 56.0 per cent.].

The chloroplatinate melts at $162-64^{\circ}$. [Found: Pt, 25.6. $(\text{C}_{11}\text{H}_{16}\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ requires Pt, 25.3 per cent.].

Like its lower homologue the pyrone forms a characteristic compound with mercuric chloride, m. p. $88-89^{\circ}$ (decomp.). (Found: Hg, 44.6. $\text{C}_{11}\text{H}_{16}\text{O}_2 \cdot \text{HgCl}_2$ requires Hg, 44.4 per cent.).

2:6-Di-n-propyl-4-pyridone.—Pure 2:6-di-n-propyl-4-pyrone was heated with strong ammonia in a sealed tube at 140° for 4 hours. On cooling the crystalline solid was filtered and recrystallised from hot water in long needles, m. p. 62° . This proved, as in the case of lower homologue, the hydrate of the pyridone. (Found: C, 66.6; H, 9.5; N, 6.7. $\text{C}_{11}\text{H}_{17}\text{QN} \cdot \text{H}_2\text{O}$ requires C, 67.0; H, 9.6; N, 7.1 per cent.).

The anhydrous pyridone was obtained by repeatedly extracting the hydrated pyridone with chloroform, and distilling under reduced pressure the resulting liquid left after removal of the solvent. It boiled between $210-15^{\circ}/12\text{mm.}$ The distillate solidified on cooling

and melted indefinitely between 85-88°. The purification of the anhydrous pyridone was met with same difficulties as in the case of its lower homologue.

The *hydrochloride* prepared in the usual way melts at 96-98°. (Found: HCl, 15.7. $C_{11}H_{17}ON$, HCl, H_2O requires HCl, 15.6 per cent.).

The *chlorplatinate* melted at 204°. [Found: Pt, 25.4. $(C_{11}H_{17}ON)_2$, H_2PtCl_6 requires Pt, 25.4 per cent.].

The author wishes to express his gratitude to the Holkar Government for providing facilities for work and to thank Mr. R. K. Aurangabadkar, M.Sc., for his valuable assistance.

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A General Synthesis of α -Unsaturated Acids from Malonic Acid. Part II.*

By MOHONLAL DALAL AND SIKHIBHUSHAN DUTT.

Malonic acid has previously been condensed with aliphatic and aromatic aldehydes in presence of glacial acetic acid or acetic anhydride with formation of alkylidene or arylidene malonic acids by various workers such as Stuart (*J. Chem. Soc.*, 1883, **43**, 403; 1886, **49**, 357), Kommenos (*Annalen*, 1883, **218**, 145) and Einhorn and Gehrenbeck (*Annalen*, 1889, **253**, 374). Riedel (*Annalen*, 1908, **361**, 89) was the first to use pyridine as the condensing agent instead of acetic acid or anhydride, and instead of getting alkylidene or arylidene malonic acids, he obtained the corresponding derivatives of crotonic or cinnamic acid with loss of carbon dioxide.

In 1925, Dutt (*loc. cit.*) showed that malonic acid condensed very easily with aliphatic and aromatic aldehydes in presence of small quantities of pyridine and piperidine. It was also found that the reaction took place in presence of pyridine alone, but the addition of small quantities of piperidine greatly accelerated the reaction, producing α -unsaturated monocarboxylic acids in excellent yields in most of the cases, with rapid loss of carbon dioxide. A large number of aliphatic and aromatic aldehydes were condensed in this way and the corresponding α -unsaturated monocarboxylic acids obtained.

On account of the interesting nature of the reaction, it was thought advisable by the present authors to study it in detail and also from the quantitative point of view. Consequently a systematic procedure was adopted. In course of these investigations it was found that the reaction was essentially a catalytic one, as without the presence of a condensing agent an aldehyde of the type of benzaldehyde condensed with malonic acid with only partial formation of benzylidene malonic acid. Not even the slightest trace of carbon dioxide was evolved. It was also found that the quantity of the catalyst had a decided influence on the vigour of the reaction and the

* Part I of this investigation has been published in *J. Indian Chem. Soc.*, 1924-1925, **1**, 297.

consequent yield of the reaction product, the best case being arrived at when the catalyst was present in the ratio of one molecule to one molecule of malonic acid. Deficiency and excess of the catalyst both seemed to diminish the yield, the former by bringing about a weak reaction and the latter by producing undesirable by-products. It was also found that *meta* and *para* compounds condensed with malonic acid giving much better yields than *ortho* compounds.

Organic bases of widely varying type have been used in bringing about condensation between malonic acid and aldehydes. As a matter of fact it has been found that practically every kind of secondary and tertiary base (primary bases cannot be used as they themselves condense with aldehydes with formation of anhydro bases) can be used in this reaction as a catalytic agent. Some of the tertiary bases used in course of this investigation (*e.g.*, dimethylaniline, diethylaniline, methylbenzylaniline, ethylbenzylaniline and quinaldine) formed simultaneous by-products (colour bases, etc.) along with cinnamic acid when benzaldehyde was used as one of the constituents of the reaction. Nevertheless, the formation of α -unsaturated acid took place inspite of the formation of large quantities of by-products.

In course of this investigation it has also been found that it is not absolutely essential to add the catalyst in the form of the free base to the reaction mixture. It can also be added in inorganic or organic acid combination. When it is in the form of an organic acid salt, the reaction takes place in the same way as if it were in the form of a free base, but when added in the form of an inorganic acid salt, the reaction is some what retarded and a higher temperature becomes necessary for the completion of the reaction (*vide* Table IV).

This investigation with widely varying types of bases was carried out in order to determine whether there was a base which could condense malonic acid with an aldehyde to a quantitative yield of the reaction product. This expectation has been realised in actual practice. The best yield was obtained in the case of lutidine which came to the theoretical. In the cases of other pyridine derivatives the yield varied between 76 and 99 per cent., whereas quinoline and its derivatives gave yields varying between 60 and 93.7 per cent. But on the other hand acridine gave only 12.2 per cent. In the case of quinaldine and 9-methylacridine the yield was abnormally reduced (23.8 per cent. and 1.5 per cent. respectively) on account of the formation of large quantities of yellow by-products (colouring matters).

Although it may be said in general that the stronger the basic character of a base, the greater is the yield of the unsaturated acid obtained by using it as a condensing agent, yet the exceptions are so numerous that such a conclusion cannot be taken with any degree of rigidity.

The following secondary and tertiary bases have been used as catalytic agents with success in the condensation of benzaldehyde with malonic acid: quinoline, isoquinoline, quinaldine, α -naphthoquinoline, β -naphthoquinoline, phenanthroline, acridine, 9-methylacridine, pyridine, α -picoline, lutidine, collidine, piperidine, dimethylaniline, diethylaniline, methylbenzylaniline and ethylbenzylaniline.

The following aliphatic and aromatic aldehydes have been condensed with malonic acid under optimum conditions using quinoline as the condensing agent: benzaldehyde, *o*-, *m*-, and *p*-nitrobenzaldehyde, *o*-chlorobenzaldehyde, *m*-, and *p*-hydroxybenzaldehyde, vanillin, *p*-dimethylaminobenzaldehyde, *p*-tolualdehyde, veratraldehyde, piperonal, anisaldehyde, furfural, citral, citronellal, cinnamaldehyde, paraldehyde, propaldehyde, isobutyraldehyde and isovaleraldehyde.

EXPERIMENTAL.

Condensation of Benzaldehyde with Malonic Acid in presence of Quinoline.

Ten different flasks fitted with air condensers and each containing benzaldehyde (6 g) and malonic acid (6 g.) were treated with quinoline as follows: first flask 1 c.c., second flask 2 c.c. and so on. The flasks were then put in a large water-bath and its temperature raised slowly. At about 50°, the contents of the flasks which had already solidified melted slowly and the evolution of carbon dioxide was noticeable at about 60°. The temperature of the water-bath was maintained at 80-85° and each flask was taken out of the bath as soon as the evolution of carbon dioxide was complete. The contents of the flasks were treated individually with dilute hydrochloric acid and then submitted to steam distillation in order to remove any unchanged benzaldehyde. The residual cinnamic acid which crystallised out on cooling was filtered off, washed with cold water, dried and weighed. The mother liquor also was treated to recover more of the product. The results are summarised in Table I.

TABLE I.

Quinoline added.	Duration of heating at 80°.	Yield in g.	Yield (%).	Quinoline added.	Duration of heating at 80°.	Yield in g.	Yield (%).
1 c.c.	10 hr.	4.6	54.8	6 c.c.	6 hr.	6.0	71.4
2	9	4.97	59.2	7	6	5.67	67.5
3	9	6.17	73.4	8	6	5.55	66.07
4	9	6.7	80.0	9	5	5.32	63.8
5	6	6.1	72.7	10	5	4.54	54.0

Condensation of o-Nitrobenzaldehyde with Malonic Acid in presence of Quinoline.

o-Nitrobenzaldehyde (4.5 g.) and malonic acid (3 g.) were condensed together in presence of quinoline in a manner similar to the above. The results are summarised in Table II.

TABLE II.

Quinoline added.	Duration of heating at 80°.	Yield in g.	Yield (%).	Quinoline added.	Duration of heating at 80°.	Yield in g.	Yield (%).
1 c.c.	10 hr.	2.16	38.1	6 c.c.	6 hr.	.975	17.2
2	9	2.52	44.4	7	6	.96	16.9
3	9	2.18	38.4	8	6	.96	16.9
4	9	1.57	27.7	9	5	.96	16.9
5	6	1.32	23.28	10	5	.86	15.17

The condensations of malonic acid with other aldehydes were carried on in similar manner using the most suitable quantities of quinoline (1 mol. of the aldehyde to 1 mol. of quinoline) in order to get the best possible yield. The results are summarised in Table III.

TABLE III.

Name of the aldehyde condensed.	Product.	Time taken for the reaction to complete.	Yield (%)
Benzaldehyde	Cinnamic acid	7 hr.	80.0
<i>o</i> -Nitrobenzaldehyde	<i>o</i> -Nitrocinnamic acid	9	44.4
<i>m</i> -Nitro- ,,	<i>m</i> -Nitro ,, ,,	3	82.5
<i>p</i> -Nitro ,,	<i>p</i> -Nitro- ,, ,,	3	75.0
<i>o</i> -Chloro- ,,	<i>o</i> -Chloro- ,, ,,	8	71.1
<i>p</i> -Hydroxy- ,,	<i>p</i> -Hydroxy- ,, ,,	10	10.6
<i>m</i> -Hydroxy- ,,	<i>m</i> -Hydroxy- ,, ,,	10	70.0
Vanillin	Ferulic ,,	8	50.3
<i>p</i> -Dimethylamino-benzaldehyde	<i>p</i> -Dimethylamino-cinnamic acid	6	68.8
<i>p</i> -Tolualdehyde	<i>p</i> Methylcinnamic acid	1	69.9
Anisaldehyde	<i>p</i> -Methoxy- ,, ,,	5	72.3
Veratraldehyde	Dimethylcaffeic ,,	4	69.5
Piperonal	Piperonalacrylic ,,	1	60.9
Furfural	Furfuralacrylic ,,	4½	66.4
Citronellal	Citronellal-acrylic ,,	8	37.8
Citral	Citralidenemalonic ,,	5	74.2
Cinnamaldehyde	Cinnamylidene- ,, ,,	5	76.5
Paraldehyde	Crotonic acid	8	40.5
Propionaldehyde	Ethylacrylic acid	12	76.8
<i>iso</i> Butyraldehyde	<i>iso</i> Propylacrylic acid	11	38.5
<i>iso</i> Valeraldehyde	<i>iso</i> Butylacrylic acid	10	40.4

Benzaldehyde was then condensed with malonic acid using the most suitable quantities (1 mol. of the aldehyde to 1 mol. of the base) of various organic bases as condensing agents. The results are summarised in Table IV.

TABLE IV.

Condensing agent.	Optimum temperature of the reaction.	Time taken for the reaction to complete.	Yield (%).
Quinoline	80°	6 hr.	80.0
<i>iso</i> Quinoline	65°	3½	91.4
Quinaldine	80°	8	23.8
α -Naphthoquinoline	80°	7	72.0
β - " "	90°	8	60.0
Phenanthroline	65°	4	93.7
Acridine	100°	9	12.2
9-Methylacridine	97°	10	1.5
Pyridine	85°	5	76.1
α -Picoline	70°	2½	99.1
Lutidine	65°	2½	100.0
Collidine	90°	7	80.2
Piperidine	85°	6	90.0
Piperidine hydrochloride	122°	5	55.2
Dimethylaniline	85°	9	31.1
Diethylaniline	85°	8	25.2
Methylbenzylaniline	85°	10	30.2
Ethylbenzylaniline	85°	10	32.2

When no condensing agent was used, benzaldehyde condensed with malonic acid at 100° with formation of only benzylidene malonic acid, and the best yield that was obtained in course of ten experiments was 57.3 p. c. of the theoretical, by 6 hours heating. Not even the slightest trace of carbon dioxide was evolved at any time during these experiments. Raising the temperature of the reaction to even 180° did not produce any evolution of carbon dioxide or formation of cinnamic acid.

Preparation and Properties of Highly Concentrated Sols. Part I.

By R. N. MITTRA AND N. R. DHAR.

In publications from these laboratories (Dhar and Gore, *J. Indian Chem., Soc.*, 1929, **6**, 31, 641) it has been shown that the properties of colloids depend considerably on their purity. Our experimental results obtained with sols of ferric, stannic, ceric, chromic, aluminium, zirconium and thorium hydroxides of different degrees of purity show that the viscosities of these sols increase steadily with their purity even when their concentrations are practically constant. When these hydroxide sols are very pure and unstable and when the amount of adsorbed electrolyte is very small, their viscosities are enormously increased.

On the other hand, we have shown that highly purified sols of ferric, chromic, stannic, zirconium and other hydroxides become less viscous when their electric charge and stability are increased by the addition of the peptising electrolyte. Hence it appears that the increased purity of the sols is associated with greater hydration and viscosity.

The concentrations of the pure sols investigated were not high, because when the sols are highly concentrated, they are partially or completely coagulated on attempting to purify them.

We have undertaken a systematic research with the object of preparing highly concentrated sols in as pure a condition as possible. We have also investigated the properties of these concentrated sols. In this communication we are submitting some of our results with the hydroxide sols of iron, aluminium and chromium.

Ferric Hydroxide Sol.

In order to prepare a concentrated sol of ferric hydroxide, most of the methods of preparing it were investigated. It was found that the maximum concentration of the sol obtainable by the method of adding ferric chloride solution to boiling water and subsequent

dialysis was only 18 g. of ferric oxide per litre. The concentration of the sol obtainable by the addition of ammonium carbonate solution to ferric chloride solution was not also high. It was observed that the most concentrated sol was obtained by following the method of Pean de St. Gilles. A precipitate of ferric hydroxide was obtained by adding ammonium hydroxide to a cold solution of ferric chloride. It was carefully washed, freed from chloride and peptised by a minimum quantity of acetic acid. The sol thus obtained was concentrated and purified by boiling until a small amount of precipitate was formed on the top. The sol was further purified by subjecting it to hot dialysis. The concentration of the sol was determined by evaporating a definite volume of the sol in a platinum crucible and weighing it as ferric oxide after ignition. In order to determine the purity of the sol, a definite volume of the sol was coagulated by potassium sulphate, and the ferric hydroxide particles were filtered and carefully washed, and the acetic acid in the filtrate was estimated by a standard alkali. We have always expressed the purity of a sol by the ratio Fe_2O_3 / acetic acid obtained from the same volume of the sol, both the concentrations being expressed in g. moles per litre. The following are the experimental results.

TABLE I.

Concentration and purity.

		Undialysed sol.	Dialysed sol.
Fe_2O_3 (g. per litre)	...	70.2	81
Acetic acid	..	1.97	0.96
Purity	...	13.37	31.64

TABLE II.

The Coagulation time.

Sol taken each time = 1 c.c. Total volume = 20 c.c. Time = 1 hr.

Electrolyte.	Undialysed sol			Dialysed sol		
	Amount.	Ppt. conc.		Amount.	Ppt. conc.	
KCl	M/8 5.8 c.c.	0.0976 M		M/3 1.75 c.c.	0.029 M	
K_2SO_4	M/30 0.855	0.0014		M/30 0.425	0.0009	
$\text{K}_3\text{Fe}(\text{CN})_6$	M/1200 9.9	0.0004		M/1200 5.9	0.000242	
$\text{K}_4\text{Fe}(\text{CN})_6$	M/2800 4.1	0.00007		M/2800 2.7	0.00048	

The ratio of the precipitation values of mono-, bi-, tri-, and quadrivalent ions is 1394: 20·7: 6: 1 in the case of the undialysed and 604: 14·5: 5: 1 in the case of the dialysed sol.

TABLE III.

Dialysed sol.

Sol taken each time=0·5 c.c. Total volume=20 c.c. Time=1 hr.

Electrolyte.	Amount.		Ppt. Conc.
KCl	M/3	2·58 c.c.	0·043 M
K ₂ SO ₄	M/30	0·255	0·000425
K ₃ Fe(CN) ₆	M/1200	4·1	0·00017
K ₄ Fe(CN) ₆	M/2800	1·9	0·000039

TABLE IV.

Viscosity.

Conc. % (Sol)	Viscosity of un- dialysed sol.	Density of undialysed sol.	Viscosity of dialysed sol.	Density of dialysed sol.
Sol A (original)	4·8	1·067	2036	1·070
Sol A/2	28·8	1·050
Sol A/4	5·2	1·032
Sol A/8	2·15	1·020
Sol A/16	1·37	1·008
Water	1·00	

The viscosity of the dialysed sol at first changes with time and then becomes constant. The viscosity results recorded are those obtained when the viscosities become constant. In the case of sol A/2 the time taken for the flow of 7 c.c. of sol decreased from 1 min. 18 sec. to 1 min. 8 sec. and the time taken for the same volume of water is 3 sec. only and for sol A/4, the time of fall decreased from 8 min. 30 sec. to 7 min. 57·5 sec., the time taken for the same volume of water being 1 min. 35 sec. The viscosity was determined at 20° by an Ostwald viscometer. In the case of the highly concentrated sols the diameter of the capillary tube used was much greater than that of the tube used for the less concentrated sols.

Aluminium Hydroxide Sol.

In preparing a concentrated sol of aluminium hydroxide, the freshly precipitated and well washed aluminium hydroxide was peptised by the minimum quantity of acetic acid. It was slightly warmed on a water-bath until the sol was clear. This was then subjected to hot dialysis. The concentration and purity were determined as in the case of ferric hydroxide sol.

TABLE V.

Concentration and purity.

		Undialysed sol.	Dialysed sol.
Al_2O_3 (g. per litre)	...	53.6	38.4
Acetic acid	26.42	17.4
Purity	...	1.193	1.298

TABLE VI.

Coagulation.

Sol taken each time = 0.5 c.c. Total volume = 10 c.c. Time = 1 hr.

Electrolyte.	Undialysed.		Ppt. conc.	Dialysed.		Ppt. conc
	Amount.			Amount.		
KCl	3.47M	4.1 c.c.	1.42 M	3.47 M	1.5 c.c.	0.5205 M
K_2SO_4	M/30	1.7	0.0056	M/30	0.55	0.0018
$\text{K}_3\text{Fe}(\text{CN})_6$	M/150	3.7	0.0025	M/150	1.3	0.00086
$\text{K}_4\text{Fe}(\text{CN})_6$	M/240	4.7	0.0019	M/240	1.7	0.0007

Ratio of the precipitating values of the above four electrolytes in molar concentration is 747:2.94:1.3:1 with undialysed sol and 743.5:2.5:1.2:1 with dialysed sol.

TABLE VII.

Sol taken each time = 0.25 c.c. Total volume = 10 c.c. Time = 1 hr.

Electrolyte.	Amount.		Ppt. conc.
KCl	3.47 M	1.9 c.c.	0.6593
K_2SO_4	M/30	0.35	0.00116
$\text{K}_3\text{Fe}(\text{CN})_6$	M/150	0.6	0.00042
$\text{K}_4\text{Fe}(\text{CN})_6$	M/240	0.85	0.00035

TABLE VIII.

Viscosity.

Conc. (Sol)	Viscosity of undialysed sol.	Density of undialysed sol.	Viscosity of dialysed sol.	Density of dialysed sol.
Sol A	7.31	1.058	98.1	1.03
A/2	2.427	1.020	8.72	1.01
A/4	1.587	1.012	2.54	1.004
A/8	1.262	1.002	1.52	...
A/16	1.103	...	1.25	...

With the concentrated sols of aluminium hydroxide, at first the viscosity changes with time and then becomes constant.

Chromic Hydroxide Sol.

As in the case of the other two, peptisation with acetic acid was tried but it did not give satisfactory result, because when the sol was subjected to hot dialysis even in a collodion bag, hardly anything was left in the bag.

Another method was adopted in which a concentrated solution of chromic chloride was boiled and ammonium carbonate solution was added gradually till a slight amount of precipitate formed. It was then subjected to continuous hot dialysis, the temperature being kept at 70°-80°.

TABLE IX.

Concentration and purity.

		Dialysed for 3 hrs.	Dialysed for 22 hrs.
Cr ₂ O ₃ (g. per litre)	...	109	127
Cl	...	32.8	19.8
Purity	...	0.774	1.496

TABLE X.

Coagulation.

Sol taken = 0.5 c.c. Total volume = 20 c.c. Time = 1 hr.

Electrolyte.	Dialysed sol I.		Dialysed sol II.	
	Amount.	Ppt. conc.	Amount.	Ppt. conc.
KIO ₃	M/3 0.75 c.c.	0.0125 M	M/3 0.45 c.c.	0.0075 M
K ₂ SO ₄	M/30 5.3	0.0088	M/30 3.3	0.0055
K ₃ Fe(CN) ₆	M/60 5.75	0.0048	M/60 4.5	0.0037
K ₄ Fe(CN) ₆	M/80 3.5	0.0022	M/80 3.0	0.0018

Ratios of the precipitation values in molar concentration are 5.7 : 4.2 : 18 : 1 for dialysed sol I (for 3 hours) and 4.16 : 3.05 : 2.05 : 1 for dialysed sol II (for 22 hours).

TABLE XI.

Dialysed sol II.

Sol taken = 0.5 c.c. Total volume = 20 c.c. Time = 1 hr.

Electrolyte.	Amount.		Ppt. conc.
KIO ₃	M/3	0.25 c.c.	0.0041
K ₂ SO ₄	M/30	1.7	0.0028
K ₃ Fe(CN) ₆	M/60	2.3	0.0019

TABLE XII.

Viscosity.

Conc.	Viscosity of dialysed sol I.	Density of dialysed sol I.	Viscosity of dialysed sol II.	Density of dialysed sol I
Sol A	2.19	1.210	1643	1.300
A/2	1.41	1.067	21.35	1.120
A/4	1.24	1.037	5.3	1.031
A/8	1.10	1.014	2.2	...
A/16	1.04	...	1.47	...

The viscosity of concentrated sols of chromium hydroxide also changes with time in the beginning and then becomes constant.

Surface Tension.

Since the lowering of surface tension has been generally considered as typical of the lyophilic colloids, attempts have been made to determine the surface tension of these hydroxide sols with a Traube stalagmometer. As the sols were highly viscous, the time required for the formation of each drop was considerable. Due to the evaporation from the drop surface during the formation of drops, these results appear to be only comparative.

TABLE XIII.

Sol.	Density of the sols.	Surface tension of sols.	Surface tension of water.
$\text{Fe}(\text{OH})_3$	1.070	72.1	72.45
$\text{Cr}(\text{OH})_3$	1.301	72.0	72.24
$\text{Al}(\text{OH})_3$	1.031	67.1	72.94

There is only slight decrease in surface tension from that of water in the case of ferric and chromic hydroxide sols but with aluminium hydroxide sol, the fall in surface tension is quite marked. Further work is in progress.

Discussion.

. From the experimental results it will be seen that we have been able to obtain highly concentrated sols of the hydroxides of iron, aluminium and chromium. The concentrations of the sols so far are as follows:

TABLE XIV

		g. per litre.
Ferric hydroxide (dialysed)	...	81 (Fe_2O_3)
Aluminium hydroxide (undialysed)	...	53.6 (Al_2O_3)
Chromic hydroxide (dialysed)	...	127 (Cr_2O_3)

It will be interesting to note that the most concentrated sol of ferric hydroxide, that was prepared before our work, contained only 35 g. of Fe_2O_3 per litre (Geffcken, *Z. Phys. Chem.*, 1904, **49**, 297).

On comparing the precipitating concentrations of electrolytes for the undialysed and dialysed sols of $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$ it will be seen that the values in the case of the dialysed sols are less than those for the undialysed ones. Because with dialysis, the stabilising electrolytes are removed and thus the charge on the colloid decreases. In other words, the sol becomes more sensitive towards electrolytes. (Dhar and Gore, *J. Indian Chem. Soc.*, 1929, **6**, 31). Moreover it will be seen, that the ratio of the amounts of monovalent and bivalent electrolytes necessary to coagulate the sols falls off considerably on dialysis and these results are in agreement with those previously obtained by Dhar and Gore.

Influence of Concentration on the Coagulation of the Sols.

In several publications from these laboratories it has been shown that the amount of uni-univalent electrolytes, necessary for coagulation of the sols of ferric, chromic and aluminium hydroxides is greater, the greater the concentration of the sol, when the sol is coagulated by electrolytes like KCl, KIO_3 and KBrO_3 . Moreover, it was also shown that when these hydroxide sols contain appreciable amount of acids, the stability of the sol is greatly increased and increasing amounts of uni-univalent electrolytes are required for coagulation of the sol when it is diluted continuously.

It is evident from the foregoing pages that the sols studied in this paper contain acids. Appreciable amount of acetic acid is associated with the sols of ferric and aluminium hydroxides. The chromic hydroxide sol was acidic due to the presence of hydrochloric acid, so it could not be coagulated by potassium chloride. Consequently it is expected that these sols should behave abnormally towards dilution when coagulated by uni-univalent electrolytes. Our experimental results show also that the amount of KCl required to coagulate the diluted sol is greater than that required to coagulate the concentrated one. The degree of dissociation of acetic acid, which is associated with the sols increases with dilution and the amount of H ion adsorbed is more marked with the diluted than with the concentrated ones. Consequently the stability and the charge on the colloid are greater in the diluted condition than in the concentrated one.

From the results on the coagulation of chromium hydroxide sol, it will be seen that KIO_3 exerts practically the same influence as K_2SO_4 . Similar results have been obtained by Weiser and Middleton (*J. Phys. Chem.*, 1920, 24, 30). It has recently been emphasised by Dhar (*J. Indian Chem. Soc.*, 1928, 5, 58) that iodic acid and iodates contain in solution the bivalent ion I_2O_6 and that is why the coagulating power of the iodate ion is practically the same as that of the sulphate ion.

It appears that the iodate ions have marked chemical affinity for the hydroxides of iron, aluminum and chromium, because the adsorption of iodate ions is greater than that of Cl^- or SO_4^{2-} ions, under identical conditions. It has been emphasised in several publications from these laboratories that the amount of adsorption of an ion by a sol is not only controlled by the amount of the electric charge on the sol, but the chemical affinity of the uncharged particles for the ions, also plays an important part.

Viscosity.

The influence of electric charge on the viscosity of colloids has been considered by several investigators. Wo. Ostwald recognises the influence of electric charge on the viscosity of colloids in the following terms—"Every electrically charged particle induces about it an electromagnetic field which hinders its movements whether such is spontaneous or brought from without. Hardy (*Z. Phys. Chem.*, 1900, **33**, 398) observed the generation of a cataphoretic current from the fall of electrically charged particles. Smoluchowski (*Kolloid Z.*, 1916, **18**, 194) concluded that the movements of electrically charged particles of a sol causes the development of an electrical field, which hinders the flow of the sol resulting in the increment of the viscosity. Smoluchowski reported that a sol with greater electric charge shows greater viscosity than a sol containing particles of feeble electric charge. Krulyt and his coworkers (*Koll. Chem. Beih.*, 1929, **28**, 1; 1929, **29**, 413) are also of opinion that an increase in electric charge on a sol produces an increment in its viscosity.

Dhar and his collaborators have, however, shown from experimental results with no less than 30 sols that the views of Ostwald, Smoluchowski, and Krulyt are untenable. Dhar concludes that other things being identical, a decrease in the electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol. The viscosity measurements with the undialysed and dialysed sols of ferric, aluminium and chromic hydroxides show that the viscosities with a sol of feeble charge are remarkably high in comparison with that of a sol of high electric charge. These experimental results are in agreement with the views of Dhar. In measuring the viscosity of the hydroxide sols, we have observed that the time of fall through the capillary gradually decreased until a constant value is reached. Similar results showing a decrease in viscosity with increase in the shearing force with lyophilic sols like gelatin and starch were obtained by Hatschek (*Kolloid Z.*, 1913, **13**, 88). It seems probable that with repeated forcing of the highly hydrated and viscous sols through the capillary, the hydrated colloid particles are subjected to a shearing force with consequent loss of adsorbed water up to a limiting value. Banerji and Ghosh (private communication) however, ascribe this decrease of viscosity to the disturbance in the structure of the highly viscous sol.

The viscosity concentration curve has been plotted with these hydroxide sols and they are found to be very steep and logarithmic in nature. These curves are of the same nature as those obtained with typical lyophilic sols like gelatin, agar and starch. It appears, therefore, that as far as viscosity is concerned the highly concentrated sols of iron, aluminium and chromium behave like lyophilic colloids.

Arrhenius (*Medd. K. Vetensk.*, 1916, 3, no. 13) has deduced the empirical formula for the viscosity concentration relation for lyophilic sols as $\log \eta = \theta c$, where η = relative viscosity of the dispersed phase, θ = constant, and c = molecular concentration of the sol. The Arrhenius equation applies very well to our results obtained with the hydroxide sols. When the logarithm of the viscosities are plotted against the concentrations, a straight line is obtained.

In order to calculate the amount of hydration, the equations of Hatschek and Arrhenius have been utilised. The formula suggested

by Hatschek (*Kolloid-Z.* 1911, 8, 34) is $\eta_s = \frac{\eta_o}{1 - \sqrt[3]{\phi}}$ where η_s and

η_o are the viscosities of the sol and dispersion medium respectively and ϕ = effective volume of the colloid particles. The hydration factor can be calculated from the observed viscosities and from the known weight concentration ϕ' by applying the above relation of Hatschek in the following form :

$h\phi' = \left(\frac{\eta_s - \eta_o}{\eta_s} \right)^3$; h is the hydration factor by which the weight concentration must be multiplied to give the volume concentration (effective volume) which enters into the formula, i.e., $h\phi' = \phi$.

Hatschek emphasises that if this formula be applied to typical emulsoid sols of proteins, the constancy of h is maintained over a moderate range of concentrations. But the factor ϕ/ϕ' with the hydroxide sols does not show any constancy. Arrhenius (*Medd. K. Vetensk.*, 1916, 3, no. 13) deduced that for substances with very high molecular weight, the molecular concentration is given by the relation

$C = \theta \frac{100p}{100 - (n+1)p}$ where θ = constant, p = weight of the dry substance

in 100 c.c. of sol, n = hydration factor, i.e., number of grams of solvent associated with one gram of solute. He obtained constant values of n in the case of protein sols. On calculating the value of n with our sols, we find the values to be negative.

It is apparent, therefore, that the exact determination of hydration from the viscosity measurement is not possible. It may be of interest to point out here that the degree of hydration for ions as obtained by different authors by various methods, does not agree and the values are looked upon with considerable uncertainty. Hence it is not surprising that the measurement of the degree of hydration for a colloid particle, which does not represent a stable state of existence, is based on still more uncertain factors. It should, however, be borne in mind that the measurement of viscosity (though not reliable in giving us a correct value for the degree of hydration) certainly conveys a qualitative idea of the hydration of colloid particles.

Reversibility of the Sols.

A curious phenomenon has been observed in the case of these hydroxide sols. The viscous sols can be dried in air and the dry mass can be reprecipitated by cold water. Uptil now this reversibility has only been observed in the case of the typical lyophilic sols, namely gelatin, agar etc. This reversibility is most prominent with $\text{Cr}(\text{OH})_3$ sol and least in the $\text{Fe}(\text{OH})_3$ sol. When the solid dry hydroxides are placed in water, they gradually swell, become transparent and finally pass into a clear colloidal solution. Warming hinders this process. Ferric hydroxide sol when completely dried in air becomes irreversible and is not reprecipitated when put into water. The dry reversible solids have been analysed and the results are as follows:

TABLE XV.

Air dried chromium hydroxide sol.

Constituents	Percentage composition.
Cr_2O_3	44.18
Cl'	13.1
Water	42.8 ⁷

TABLE XVI.

Air dried aluminium hydroxide sol.

Constituents	Percentage composition.
Al_2O_3	55.2
Acetate	1.01
Water	44

The empirical formula derived for the dried chromic hydroxide sol from the percentage composition is $\text{Cr}_5(\text{OH})_{11}\text{Cl}_3 \cdot 28\text{H}_2\text{O}$. Bjerrum (*Z. Phys. Chem.*, 1910, 73, 724) claimed to have obtained the basic salts $\text{Cr}(\text{OH})_2\text{Cl}$ and $\text{Cr}(\text{OH})\text{Cl}_2$. The basic compound

$\text{Cr}_2(\text{OH})_{12}\text{Cl}_3 \cdot 28\text{H}_2\text{O}$ obtained by us is not mentioned in the literature. Moreover by splitting the formula in the form $[\text{Cr}(\text{OH})_3 \cdot 7\text{H}_2\text{O}]_4\text{CrCl}_3$ it is clear that one molecule of chromic chloride is associated with 4 molecules of $\text{Cr}(\text{OH})_3$ and each molecule of $\text{Cr}(\text{OH})_3$ is associated with 7 molecules of water of hydration. When viewed with a high power microscope, the dry substance appears to consist of regular layers of solid. The empirical formula of the dried aluminium hydroxide is $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{COOH}$. The dried mass of the aluminium compound is transparent and looks like glass.

In this connection it is to be noted that a high degree of hydration is not associated with the reversibility of the hydroxide sols. From our results, it will be seen that ferric hydroxide sol is more viscous than the other two at more or less the same concentration, but the property of reversibility is least developed with ferric hydroxide sol. Whilst the chromic hydroxide sol, though the least viscous and consequently the least hydrated of the three, is the most easily reversible. Kruyt and his coworkers (*Z. Phys. Chem.*, 1922, **100**, 250) have shown that hydration is closely associated with the stability of the sols towards their coagulation by electrolytes. According to these investigators, layers of water envelop the colloid particles and protect them from agglomeration on neutralisation of electric charge. Ghosh and Dhar (*J. Phys. Chem.*, 1930, **34**, 326) have shown that this view of Kruyt supported by Freundlich (*Koll. Chem. Beih.*, 1922, **16**, 234) is untenable in view of their experimental results on the coagulation of highly viscous and hydrated inorganic sols. Our results on the coagulation of these hydroxide sols also point to the fact that the conclusion of Kruyt and Freundlich and others are not justified. Thus ferric hydroxide sol has been found in these investigations to be highly hydrated, whilst the sol is the least stable of three hydroxides investigated in this paper. It seems on the other hand that the stability of a sol towards the action of electrolytes is more related with the electric charge on the colloid particles than with its hydration. Chromic hydroxide sol, which contains a large amount of chromic chloride, is necessarily less viscous and hydrated because of the comparatively high electric charge on the particles and is most stable amongst these three hydroxide sols. We are of opinion that high viscosity and hence greater hydration are not necessarily a cause of stability of the sols towards their coagulation.

Summary.

1. Highly concentrated sols of ferric, chromic and aluminium hydroxides have been prepared. The concentrations being 81 g. (0.5063 gram mole) Fe_2O_3 per litre, 53.6 g. (0.5255 gram mole) Al_2O_3 per litre and 127 g. (0.8356 gram mole) Cr_2O_3 per litre.

2. These hydroxide sols of iron, aluminium and chromium could not be completely freed from the peptising substances even by hot dialysis. It has been found that if the dialysis be carried beyond the purity mentioned, the hydroxides set to firm jellies.

3. The undialysed sol of the same concentration is more stable, towards electrolytes than the dialysed ones. The ratio of the precipitating concentrations of uni- to bivalent ions decreases as the purity of the sol increases.

4. The viscosity of the sols is exceedingly high in the concentrated condition and increases with purity even their when concentrations are practically identical. The results of viscosity measurements show that the less the charge on a colloid, the greater is its viscosity. These results are in agreement with the views of Dhar that the viscosity of a colloid increases as the charge decreases.

5. The viscosity concentration curves with these hydroxide sols are very steep and resemble those obtained with typically lyophilic sols.

6. Preliminary measurements of surface tension show that the values of the surface tension of ferric and chromic hydroxide sols are slightly less than that of water but in the case of aluminium hydroxide, the fall in surface tension is quite marked.

7. The highly concentrated sols of aluminium and chromium hydroxide behave as reversible colloids in as much as the air dried solids obtained from these sols swell and again pass into colloidal condition when kept in contact with water.

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Some Observations on Selenium and Selenium Dioxide and the Oxides of Nitrogen.

By EDWARD BARNES

No observations appear to have been recorded on the action of NO on Se or SeO_2 , nor on the reactions between NO_2 , and Se and SeO_2 , except the one referred to in section III. The following observations, made by the author, may therefore be worth putting on record.

I. *Selenium Dioxide and Nitric Oxide.*

Selenium dioxide is fairly easily reduced to elementary selenium, and so it often behaves as a mild oxidising agent. It was expected, therefore, that it would react with nitric oxide. The subject was studied experimentally as follows. A long glass tube, of about 1.5 cm. bore and constricted at about the middle, was sealed on to a vacuum tap at one end. Some selenium was placed in the open half of the tube and oxidised to SeO_2 by heating in a stream of dry oxygen which was mixed with some dry NO_2 , obtained by heating dry lead nitrate contained in a side-tube. Some of the SeO_2 was then sublimed into the other part of the tube, and the tube was drawn off and sealed at the constriction. This procedure was adopted because of the highly hygroscopic nature of SeO_2 . After closing the tap, this tube was sealed on to an all-glass apparatus consisting of a Töpler pump and mercury gas-holder containing dry nitric oxide. After completely evacuating the tube containing the SeO_2 , it was filled with NO at atmospheric pressure. No immediate reaction occurred, and after leaving for a week at room temperature (30° .) the gas remained colourless and the white needles of SeO_2 remained unchanged. The tube was then slowly heated, but no reaction occurred up to the sublimation temperature of SeO_2 (about 315°). It was found that SeO_2 could be sublimed unchanged in an atmosphere of nitric oxide. During sublimation the SeO_2 gave its characteristic greenish-yellow vapour, but as soon as this had condensed, the gas in the tube was seen to be colourless and the sublimate was snow-white. The gas was pumped out of the tube and found to be unchanged NO.

II. *Selenium and Nitric Oxide.*

A tube of about 50 c.c. capacity, closed at one end and sealed on to a vacuum tap at the other, was sealed on to the Töpler pump and mercury gas-holder containing NO. The tube contained 2.3 g. of dry amorphous selenium. The Se was prepared, by passing SO_2 into a solution of pure selenious acid to which some HCl had been added, filtering, washing repeatedly with water, and drying in *vacuo* over concentrated H_2SO_4 . The tube was evacuated completely, heated in an electric tube-furnace, and filled with NO. Several experiments were carried out and it was found that no reaction took place between selenium and nitric oxide up to a temperature of 330° . After several hours at this temperature, the selenium had distilled to the cooler end of the tube and condensed there as opaque black drops. After the experiments, the gas was pumped out and found to be unchanged NO by absorption by Diver's reagent (alkaline sulphite solution). Experiments were not carried out at higher temperatures as, with the arrangement used, the selenium would have simply distilled into the connecting tube outside the heater.

III. *Selenium and Nitrogen Tetroxide.*

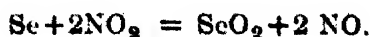
The only reference to this subject that has been found is in a paper by Jannek and Meyer (*Ber.*, 1913, **46**, 2876). These workers, for determination of atomic weight, prepared pure SeO_2 by passing a stream of oxygen mixed with some NO_2 over heated selenium. It has been known since the time of Barzelius' investigations on selenium that selenium is oxidised by oxygen much more readily in the presence of nitric acid vapour. Jannek and Meyer (*loc. cit.*) explain this as being due to a reaction similar to that taking place in the Lead Chamber Process, the NO acting as oxygen-carrier. In support of this view they state that they had found that when NO_2 is led over powdered Se, it is reduced to NO, but they give no experimental details except that the reaction occurs at ordinary temperatures and better at higher temperatures well below the melting point of selenium.

A series of experiments was carried out in order to investigate this reaction. Owing to the nonavailability of liquid air, the arrangement described below was used. Dry liquid nitrogen tetroxide was sealed into a number of small capsules which were drawn out to fine

capillaries at one end. The NO_2 was prepared by Cundall's method. One arm of a T-piece was fused to a closed glass tube of about 200 c.c. capacity. This tube contained several grams of dry amorphous selenium spread along its length and it was supported in a horizontal position. Another arm of the T-piece was fused on to a tap (A) which led through a tube of powdered NaOH to the Töpler pump. The third arm of the T-piece was also fused on to a tap (B). This tap was placed in the "open" position and one of the capsules of NO_2 was introduced into its open end so that the capillary of the capsule passed into the bore in the key of the tap. The open end of the tap was then drawn off and sealed after introducing some glass-wool to prevent the capsule from becoming heated. In order to prevent the possibility of the NO_2 acting on tap-grease, the taps were lubricated with gummy metaphosphoric acid which was protected from atmospheric moisture by an external layer of vaseline. After completely evacuating, tap A was closed and by slightly turning tap B, the capillary end of the NO_2 capsule was broken off and the nitrogen tetroxide rapidly vaporised into the reaction vessel containing the selenium, which was kept at 30° . No visible signs of action were seen on first contact. By observing the colour of the gas at intervals, as seen through a layer 25 cm. thick against a white background, a slow fading of colour was found to occur, and after 48 hours the gas had become quite colourless. The gas was then pumped out and analysed. It was found to be practically pure nitric oxide. The contents of the reaction tube were now treated with water to dissolve out the SeO_2 formed. This solution was filtered and treated with SO_2 to decompose the selenious acid, and the precipitated Se was collected in a Gooch crucible and weighed. The figures obtained in one of these experiments are as follows

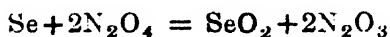
	Found.	Calculated.
Weight of NO_2 used	0.302	0.293
Weight of Se collected	0.252	0.252
Volume of NO at N.T.P.	141.2 c.c.	142.7 c.c.

The volume of NO stated is the volume of gas absorbed by the alkaline sulphite. 0.77 C.c. remained unabsorbed; this may have been nitrogen formed by complete reduction of NO_2 . The values given in the second column are calculated from the equation



The approximate agreement of these numbers with those found shows that this equation represents the reaction that occurs to the extent of about 97 per cent. The result recorded in section I shows that this reaction is not reversible within the temperature range mentioned.

The reaction of selenium with liquid nitrogen tetroxide was also studied. Some liquid nitrogen tetroxide was prepared by Cundall's method, purified by being passed through tubes containing heated As_4O_6 and anhydrous CuO , and dried by P_2O_5 . It was then distilled over P_2O_5 into a stoppered tube through a side arm which was then drawn off and sealed. This tube was kept at 0° by placing it in a vacuum flask containing ice and water. On adding some dry amorphous selenium, the light yellow liquid became slightly green. After some minutes, it was bright green and after several hours greenish blue. The tube was kept at 0° for several days. No effervescence was observed and no noticeable pressure was generated, indicating that no appreciable amount of nitrogen was formed. The tube was then allowed to warm and the oxides of nitrogen to escape. The residue consisted of SeO_2 with an appreciable amount of unchanged Se . On treating with water and filtering, a solution of selenious acid free from selenic acid was obtained. This experiment shows that the reaction between selenium and liquid nitrogen tetroxide may be represented by the equation



IV. *Selenium Dioxide and Nitrogen Tetroxide.*

The experiments described in the previous section indicate that the reaction between selenium and nitrogen tetroxide takes place slowly. The slowness of the reaction is probably not due to the reaction itself but to the layer of SeO_2 that soon covers the surface of the selenium and prevents further contact. This layer of SeO_2 is apparently insoluble in liquid nitrogen tetroxide as the following experiment shows. Some SeO_2 was sublimed in to the bottom of a U-tube, one arm of which was sealed, and then some nitrogen tetroxide was condensed in it. After placing a plug of glass-wool halfway down the open arm of the U-tube, it was sealed off. After leaving the SeO_2 and liquid NO_2 in contact for 24 hours, the U-tube was inverted so as to filter the liquid through the glass wool into one closed end of the

U-tube. The other end of the U-tube was now cooled in a freezing mixture so as to cause the NO_2 to distil over. The process was hastened by slight warming. No residue of SeO_2 remained after the NO_2 had distilled over. There was no indication that these two compounds combine to form a double compound.

V. *Selenium and Nitric Acid.*

It is well-known that the oxidising action of ordinary nitric acid on elements is, in some cases, due to the catalytic action of NO_2 present as an impurity. The pure acid is often without action, as in the case of copper. It was thought that this might be the case with selenium as it has been shown that Se is acted upon by NO_2 . Some of the purest obtainable strong nitric acid was treated with 5 per cent. of its weight of urea so as to remove any NO_2 present. When some amorphous selenium was added to this acid, there was an immediate and vigorous reaction. Nitric acid therefore appears to react with selenium in the absence of nitrogen tetroxide.

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Influence of Stirring on the Velocity and Temperature Coefficient of Photochemical Reactions.

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Attempts have been made from time to time to find out whether the velocity of a homogeneous photochemical reaction is affected by shaking or stirring the reacting substances. So far however, no conclusion has been arrived at from theoretical considerations. In this communication we shall consider this problem from the laws of absorption of light.

Let us consider an absorbing media of thickness l , and I_x be the intensity of light after its passage through the length x of the medium. The amount of the light absorbed

$$= I_o - I = I_o (1 - e^{-k'l}) \quad \dots \quad (1)$$

Hence the light absorbed per unit length $= \frac{I_o(1 - e^{-k'l})}{l}$.

If the velocity of the reaction is proportional to the n^{th} power of the light absorption, the average velocity

$$= y_1 = k \left\{ \frac{I_o(1 - e^{-k'l})}{l} \right\}^n \quad \dots \quad (2)$$

This is the average velocity for a reaction, in which the reacting substances are well stirred. If there is no stirring, the velocity of the reaction will vary from place to place with the thickness of the medium according to the variation in light absorption with the thickness of the mixture as given by Lambert's law of absorption. The reaction takes place not only at the places of maximum absorption, but also at places of low absorption, so that the observed velocity is the mean of these velocities at various points along the thickness of the solution. The amount of light absorption by an unit surface

of the solution situated between l and $l+dl$ along the length of the solution is given by

$$I_l - I_{l+dl} = I_0 \{e^{-kl} - e^{-k(l+dl)}\} \quad \dots \quad (a)$$

We can expand this by applying Taylor's theorem

$$f(x+dx) = f(x) + f'(x)dx + \frac{f''(x)d^2x}{2} \dots\dots\dots$$

$$\text{Hence } I_l - I_{l+dl} = -I_0 f(e^{-kl})dl = I_0 k e^{-kl} dl \quad \dots \quad (b)$$

The absorption per unit length between l and $l+dl$

$$= \frac{I_0 k e^{-kl} dl}{dl} = k e^{-kl} I_0$$

Hence the velocity of the reaction at this place is equal to

$$k_1 (I_0 k e^{-kl})^n.$$

If V_2 be the mean average velocity and v_1, v_2, v_3 , etc., be the velocities at different points along the length of the solution of thickness l , then

$$\begin{aligned} V_2 \times l &= v_1 dl + v_2 dl + v_3 dl + \dots\dots\dots \\ &= \int_{l=0}^{l=l} k_1 (I_0 k e^{-kl})^n dl = \int_{l=0}^{l=l} k_1 I_0^n k^n e^{-kn l} dl \\ &= k_1 I_0^n k^n \left[\frac{e^{-kn l}}{-kn} \right]_{l=0}^{l=l} = k_1 I_0^n k^n \left[\frac{1}{kn} - \frac{e^{-kn l}}{kn} \right] \\ &= \frac{k_1}{k \cdot n} I_0^n k^n \left[1 - e^{-kn l} \right] = \frac{k_1}{n} I_0^n k^{n-1} \left[1 - e^{-kn l} \right]. \end{aligned}$$

Hence the average velocity without stirring is equal to

$$V_2 = \frac{k_1 I_0^n k^{n-1}}{n} \left[1 - e^{-kn l} \right] \quad \dots \quad (3)$$

If the reaction velocity is directly proportional to the light absorption, then $n=1$ and hence

$$V_1 = V_2 = \frac{k_1}{l} I_0 (1 - e^{-kl})$$

or the stirring produces no effect on the velocity of the reaction, and hence on the temperature coefficient. If n is less than unity, then $V_1 \neq V_2$ or

$$k_1 \left\{ \frac{I_0(1-e^{-kl})}{l} \right\}^n \neq \frac{k_1}{nl} I_0^n (1-e^{-kl})^{n-1}.$$

From considerations based on the principles of inequalities, it can be proved that when n is less than 1 then

$$k_1 \left\{ \frac{I_0(1-e^{-kl})}{l} \right\}^n > \frac{k_1}{nl} I_0^n k^{n-1} (1-e^{-kl})$$

for all values of k and l . This shows that the velocity of the reaction for a continuously stirred reaction is greater than the velocity when the substances are not stirred.

In several papers published from our laboratories, it has been shown that the temperature coefficient of a photochemical reaction depends on its acceleration caused by light. The greater the acceleration, the smaller is the temperature coefficient. Hence the temperature coefficient for the reaction with good stirring which has got higher photochemical acceleration must be less than that for the same reaction when not stirred. This is what has been actually observed. Two interesting cases of variation in the velocities may be considered: (1) when the absorption is low and (2) when the absorption is very high. When the absorption is very high, $kl = \infty$ and $e^{-kl} = 0$. When the absorption is very low e^{-kl} can be expanded. Thus for continuous stirring we get from (a)

$$V_1 = k_1 \left(\frac{I_0}{l} \right)^n$$

and for the unstirred reaction we have

$$V_2 = \frac{k_1}{nl} I_0^n k^{n-1}.$$

Hence

$$\begin{aligned} \frac{V_1}{V_2} &= \frac{k_1 \left(\frac{I_0}{l} \right)^n}{\frac{k_1}{nl} I_0^n k^{n-1}} = \frac{k_1 I_0^n l^n}{k_1 I_0^n l^n k^{n-1}} = \frac{l^n}{l^{n-1} k^{n-1}} \\ &= n \cdot (kl)^{1-n} \quad \dots \quad \dots \quad (A) \end{aligned}$$

but $kl = \infty$. Or the ratio of these two velocities of stirred and unstirred reaction is very high and hence there must be marked variation in temperature coefficients in the two cases.

When the absorption is very low

$$e^{-kl} = 1 - kl + \frac{(kl)^2}{1.2} - \frac{(kl)^3}{1.2.3}$$

Then for the stirred reaction

$$V_1 = k_1 \left\{ \frac{I_o(1 - 1 + kl)}{l} \right\} = k_1 k^n I_o^n$$

and for unstirred reaction,

$$\begin{aligned} V_2 &= \frac{k_1}{nl} I_o^n k^{n-1} \left\{ 1 - 1 + knl \right\} \\ &= \frac{k_1}{nl} I_o^n k^n nl = k_1 I_o^n k^n. \end{aligned}$$

Hence

$$\frac{V_1}{V_2} = \frac{k_1 k^n I_o^n}{k_1 k^n I_o^n} = 1 \quad \dots \quad \dots \quad (B)$$

or the velocity of the unstirred reaction is the same as the velocity of the same reaction when stirred. Thus the ratio of the two velocities can vary from infinity to unity depending on the amount of absorption. This clearly shows that what a great amount of variation in temperature coefficient of a photochemical reaction is possible under the two circumstances, when the velocity of the reaction is not directly proportional to the light absorption. The equation shows that the velocity of a reaction under both the circumstances depends on the thickness of the solution. The greater the length of the solution, the smaller is the average absorption and hence the velocity is small.

Moreover the shape of the vessel in which the solutions are exposed to light also exert a marked effect on the absorption and on the velocity of the reaction. This leads to a variation in the temperature coefficient with change in the size and shape of the reaction vessel. Hence whenever the results of two workers on the

same reaction are to be compared and when the reaction is not directly proportional to the light absorption, attention should be paid to their experimental conditions as regards the thickness and the shape of the reaction vessel.

The observations of Bhattacharya and Dhar that the relation between intensity and velocity for a particular reaction is not a constant factor but depends upon the amount of photochemical acceleration is highly interesting from the above viewpoint. As the absorption decreases, the photochemical acceleration falls, and the relation between intensity and velocity approaches direct relationship or the effect of stirring goes on decreasing till with very small absorption, the stirring has got practically no effect. This is what is actually expressed by $v_1/v_2=1$ for small absorptions, when n approaches unity.

Regarding the experimental confirmation of the foregoing deductions the only experiments performed are those by Young and Style (*Trans. Faraday Soc.*, 1931, **27**, 494) on the influence of stirring on the photochemical reaction between iodine and potassium oxalate. They have observed a marked decrease of the temperature coefficient when the mixture is well stirred.

We have also studied the influence of stirring on the velocity of the same photochemical reaction and we have observed that the velocity of the reaction is increased on stirring.

Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307), Briers, Chapman and Walters (*J. Chem. Soc.*, 1926, **129**, 526) and Mukerji and Dhar (*J. Phys. Chem.*, 1928, **32**, 1308) observed that the reaction between potassium oxalate and iodine and ammonium oxalate and iodine is nearly proportional to the square root of the incident radiation. Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 473) have shown for the same reaction that when the photochemical acceleration is not large and an aqueous solution of iodine is used and KI is not added and the mixture is illuminated by radiations

of wave-lengths 5650\AA , and 7304\AA , the reaction tends to be directly proportional to the light intensity. We are investigating the influence of stirring under the conditions when the reactions tend to be directly proportional to light intensity and we expect to get only very slight variation of the velocity of the reaction with stirring. We are also investigating the influence of stirring on other photochemical reactions.

Summary.

We have deduced from the laws of light absorption a relation which states that when the relation between the light absorption and velocity of the reaction deviates markedly from unity, stirring will lead to increased velocity and decreased temperature coefficient. When the relation between intensity and velocity of the reaction is unity, stirring should have no effect on the velocity and temperature coefficient.

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A Magnetic Study of the Colour Changes in Cobalt Chloride.

By S. S. BHATNAGAR AND A. N. KAPUR.

The well-known and striking colour changes red \rightleftharpoons blue of cobalt chloride solutions have led to considerable controversy. Numerous early investigators (Babo, *Jahresber.*, 1857, 72; Schiff, *ibid.*, 1859, 52; Gladstone, *J. Chem. Soc.*, 1858, 10, 79; 1859, 11, 36; Russell, *Proc. Roy. Soc.*, 1881, 32, 253; Hartley, *Sci. Proc. Roy. Dubl. Soc.*, 1900, ii, 7, 253; etc.) have endeavoured to explain the colour changes entirely in terms of varying hydration of the cobalt chloride. The explanations of the colour phenomena by Engel (*Bull. Soc. chim.*, 1891, iii, 6, 239) on the concept of double salts in solution and by Ostwald from single ionic standpoint are both untenable.

Donnan and Bassett (*J. Chem. Soc.*, 1902, 81, 939) explained the colour changes on the basis of some such equilibrium as



Hartley (*J. Chem. Soc.*, 1903, 83, 401) considered that $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and CoCl_2 were formed on heating aqueous solutions of cobalt chloride. Lewis (*Z. Phys. Chem.*, 1905, 52, 224), Jones and Bassett (*Z. Phys. Chem.*, 1905, 52, 231) and Hulbert, Hutchinson and Jones (*J. Phys. Chem.*, 1917, 21, 150) have also explained the colour changes entirely in terms of hydration theory.

Moore (*Z. Phys. Chem.*, 1906, 55, 641) from his spectroscopic measurements considers the existence of complex ions very probable. Brown (*Proc. Roy. Soc. Edin.*, 1912, 32, 50) on the other hand, from his measurements on absorption of light by cobalt chloride solutions favours the hydration theory.

Denham (*Z. Phys. Chem.*, 1909, 55, 641) from measurements of transport numbers concluded that "auto-complexes" were present in solutions of cobalt bromide.

Gröth (*Z. anorg. Chem.*, 1925, 146, 305) from molecular extinction coefficients supports the assumption of an equilibrium



the blue colour of the solutions being due to the complex ion CoCl''_4 . Gróh and Schmid (*ibid.*, 1927, **162**, 321) came to the same conclusion from observations on the solubility of lithium chloride in acetone solutions of cobalt chloride.

Kotschubei (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055) studied the water carried by the ions by Nernst's method, using phenols as the indicator. He found that the hydration of the cobalt ion and of undissociated cobalt molecules diminished with increase of concentration and rise of temperature, and considered that the change was probably from $\text{Co}(\text{H}_2\text{O})_6''$ to $\text{Co}(\text{H}_2\text{O})_4''$ and $\left[\text{Co} \begin{smallmatrix} (\text{H}_2\text{O})_2 \\ \text{Cl}_2 \end{smallmatrix} \right]$ and not to CoCl''_4 .

Hill and Howell (*Phil. Mag.*, 1924, *vi*, **48**, 833) suggested that whether cobalt compounds are red or blue depends upon the state of co-ordination of the cobalt atom; if this is surrounded by six other groups or atoms, a red colour results, while if there are only four groups or atoms, the colour is blue.

Bassett and Croucher (*J. Chem. Soc.*, 1930, 1784) fail to reconcile this view with the electrical evidence as to the nature of the red and blue solutions. They conclude that colour is independent of the state of co-ordination.

It is evident from the above resumé of the subject that the theory of the constitution of cobalt salts in solution is far from satisfactory. The magnetic properties of the salts in solution would naturally suggest themselves to investigators as likely studies which would shed a flood of light on the subject.

The magnetic behaviour of cobalt salts in solution is in itself quite complicated. With concentration of the chloride ranging from 0.5 to 0.005 g. mols per litre, Trumpler and Cabrera (*J. Phys. Radium*, 1922, *vi*, **3**, 443), obtained values for p lying between 24.53 and 24.59. With the addition of hydrochloric acid, Cabrera (*loc. cit.*) found that the equilibrium between the different ionic carriers was displaced in a direction which suggested that there may also be carrier of moment less than 23 Weiss magnetons.

Chatillon (*Ann. Physique*, 1928, **9**, 187), found for aqueous solutions of CoCl_2 , CoSO_4 and $\text{Co}(\text{NO}_3)_2$, a value of 25.02 for the Weiss magneton number. In amyl alcohol and ethyl alcohol cobalt chloride gave the value of 23 for p , the Weiss magneton number and the aqueous solutions of CoCl_2 diluted with hydrochloric acid gave results depending on the concentration of the acid. It appears that similar

solutions do not always give the same results ; the temperature variation is linear only over a limited range and magneton numbers 22, 23, 24, 25 and 26 were found.

From the above it is clear that the magnetic behaviour of the cobalt salts in solution is very complicated. In this paper we have determined

(a) The value of p , the Weiss magneton number, for the cobalt salts in aqueous solutions, and

(b) The variation of p , with concentration for various hydrates of cobalt chloride in different solvents.

From these and from the results of other investigations, we have attempted to clarify our views regarding the constitution of cobalt salts in solution.

EXPERIMENTAL.

The apparatus employed during this investigation was in principle similar to Bauer and Piccard's U-tube type and is fully described in a previous paper (Bhatnagar, Mathur and Mal, *Phil. Mag.*, 1930, vii, 10, 101) from this laboratory.

As in the original method of Bauer and Piccard (*J. Phys. Radium*, 1920, vi, 1, 97) the meniscus, after putting on the field, could be brought back to the initial position by raising or lowering the reservoir and the rise or fall read on a fine micrometer. These readings were checked with those taken directly on a travelling microscope.

Now, according to the well-known expression, the specific mass susceptibility is given by

$$\chi = \frac{2\theta g}{H^2} + \chi_o \frac{\rho_o}{\rho}$$

where χ_o = specific susceptibility of air (21.0×10^{-6}),

ρ_o = density of air at the given temperature and pressure,

ρ = density of substance under investigation,

θ = rise or fall of the meniscus.

The apparatus was standardised with respect to water ($\chi = -7.25 \times 10^{-7}$).

Salts.

Pure specimens of Kahlbaum's were taken and their purity determined by ordinary methods of chemical analysis.

From the mass susceptibilities of the salt solutions as calculated from the expression given above, the volume susceptibilities were calculated. The mass susceptibility of the salt is given by the expression:

$$\chi_{\text{salt}}'' = \chi_{\text{solution}}'' - \chi_{\text{air}}'' - \left(\chi_{\text{solvent}}''' \times \frac{W_{\text{solvent}}}{1000} \right) \quad \text{and } \chi_M,$$

$$\frac{W_{\text{solute}}}{1000}$$

the gram molecular susceptibility is given by $\chi_M = \chi_{\text{salt}}''' \times \text{M. wt.}$

The Curie constant C_M was calculated from $C_M = \chi_M \cdot T$ where T is the absolute temperature. The Weiss relation $C_M = \chi_M (T - \theta)$ could not be employed as the range of temperatures investigated was not large enough to extrapolate the value of θ .

Then p , the number of Weiss magnetons is given by $p = 14.07 \sqrt{C_M}$.

TABLE I.

Condition in which Co ion is placed.	Moments in magnetons.	Reference.
Aqueous solution of		
Co(NO ₃) ₂	25.05	Present work
	25.02	Chatillon (<i>loc. cit.</i>)
CoCl ₂	25.04	Present work
	25.05	Chatillon
CoSO ₄	25.04	Chatillon
CoCl ₂ · 6H ₂ O (solid)	25.03	Chatillon
CoCl ₂ · 2H ₂ O (solid)	25.02	Present work
Anhydrous CoCl ₂	24.96	Theodorides (<i>J. Phys. Radium</i> , 1922, vi, 3, 1)
Anhydrous CoSO ₄	25.06	Do
	24.95	
CoSO ₄ calcined at temperature lower than 400°.	25.07	Chatillon
CoSO ₄ calcined at dull red heat.	25.98	Miss Serres (<i>Compt. rend.</i> , 1925, 181, 714)
	25.98	Chatillon

TABLE II.

Condition in which Co ion is placed.	Moments in magnetons.	Reference.
Solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in ethyl alcohol		
12.519 g. per 100 g.	22.48	
4.459 " " " "	22.23	Present work
CoCl_2 in ethyl alcohol	23.00	Chatillon
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in methyl alcohol		
10.86 g. per 100 g.	23.00	
8.55 " " " "	22.75	Present work
4.588 " " " "	24.42	
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in methyl alcohol	23.02	Present work
Solutions of CoCl_2 in amyl alcohol	23.04	Chatillon
	23.01	Present work
Solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in a mixture of ethyl and amyl alcohol	23.08	Present work
CoCl_2 crystallised in absolute alcohol	26.02	Chatillon

TABLE III.

Condition in which Co ion is placed.	Moments in magnetons.	Reference.
Solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mixed with HCl	25.07	
	23.47	
Varying concentrations of HCl	23.52	Chatillon
	23.46	
	22.03	
	21.97	
Solution of CoCl_2 in concentrated sulphuric acid	25.66	Foex (<i>Trans. Amer. Electrochem. Soc.</i> , 1929, 55, 97)

Summary and Discussion of Results.

Table I confirms the conclusions of Chatillon that in all aqueous solutions of cobalt salts, the value of the Weiss magneton number is 25. From a comparison of this value to the values of p , the Weiss magneton, found by other investigators for different salts of cobalt in the solid state, it appears that the normal value for the red Co^{++} ion is 25.

Table II gives the values of the Weiss magneton for solutions of different hydrates of cobalt chloride in ethyl, methyl and amyl alcohols. It is interesting to note that when $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in ethyl alcohol, the value of p varies between 22 and 23 according to the concentration of the solution and it never reaches as high as 25 which is the established normal value for aqueous solu-

tions. Similar results have been obtained in methyl alcohol and amyl alcohol solutions.

If the paramagnetic ions in solution remain all of one kind, the value of p shall also remain constant. But if ions characterised by different Weiss magneton values p_1, p_2, \dots, p_n are present, then the value of p is given by

$$p^2 = \frac{1}{n} (n_1 p_1^2 + n_2 p_2^2 + \dots)$$

where n_1, n_2, \dots give the relative number of ions of Weiss magneton values p_1, p_2, \dots and $n = n_1 + n_2, \dots$. And as variations in concentrations of a solution change the relative values of n_1, n_2, \dots , a variation in the values of p with concentration of the solution must take place. The fact that the alcoholic solutions of cobalt salts have colours varying from blue-violet to pink, would suggest the presence of different ionic carriers, which would result in variation of p with concentration. We find from our results that the value of p does change with concentration.

When we examine these results with those obtained by Chatillon for $\text{CoCl}_2, 6\text{H}_2\text{O}$ in HCl solutions we are immediately struck by the remarkable fact that in all these cases the value of p falls from 25 to a figure between 22 and 24. This fall in the value of p from 25 to somewhere between 22 and 24 is not due to the production of the anhydrous CoCl_2 as suggested by Lewis (*loc. cit.*), Jones and Bassett (*loc. cit.*) or to $\text{CoCl}_2, 2\text{H}_2\text{O}$ as suggested by Hartley (*loc. cit.*), as the value of p for both these salts is approximately 25, the usual value for cobalt salts. The addition of HCl will result in formation of ions of the $(\text{CoCl}_3)'$ and $(\text{CoCl}_4)''$ type and it is clear that the addition of Cl' to the CoCl_2 will have the effect of bringing down the value of p , as happens to be the case.

That the decrease of the Weiss magneton value for the cobalt salts in alcoholic and HCl solutions cannot be explained on the production of anhydrous or dihydrate CoCl_2 is further proved by the observation of Foex (*loc. cit.*) that the value of p for cobalt chloride in concentrated sulphuric acid is 25.66 and not between 22 and 23 as it should have been if the simple hydration theory were true.

Magnetic Properties of Solid Solutions.

By S. S. BHATNAGAR AND PYARA LAL KAPUR.

Homogeneous crystals containing two salts mixed in indefinite proportions and formed in solutions containing a mixture of both salts were called "Mixed crystals" by Roozeboom (*Z. Phys. Chem.*, 1890, **30**, 385) and named solid solutions by Van't Hoff (*Z. Phys. Chem.* 1890, **5**, 322) because they showed great resemblance in their behaviour to ordinary liquid solutions, and obeyed the laws applicable to them. Doubts have been expressed by Kuster (*Z. Phys. Chem.*, 1895, **17**, 367), Lehmann (*Ann. Physik*, 1894, **51**, 67), Ruzicka (*Z. Phys. Chem.*, 1910, **72**, 381) and Von Weimarn (*Kolloid Z.*, 1910, **7**, 35) as to whether it is right that these isomorphous mixtures should be considered as solid solutions at all. This position cannot be maintained any longer, for it has been shown by Bruni and Meneghini (*Atti. R. Accad. Lincei.*, 1911 (5), **20**, i, 671, 927), Sirovich and Cartoceti (*Gazzetta*, 1922, i, **52**, 436) and Desch (*Brit. Assoc. Reports*, 1912, 348) that diffusion, a process regarded as characteristic of the gaseous state and that of solution, takes place not only in the case of crystalline metals, but also in the case of mixed crystalline salts like sodium chloride—potassium chloride, potassium chloride—potassium bromide, etc. Moreover, Tamman (*Nachr. Ges. Wiss. Gottingen*, 1916, 119) has shown that when mixed crystals of gold and copper, or of gold and silver, are treated with reagents which are solvents for one of the components, they do not behave as if they were heterogenous mixtures. Finally, x-ray examination of the mixed crystals of potassium bromide—potassium chloride and of potassium bromide—ammonium bromide, etc., by Vegard and Schjelderoy (*Physikal. Z.*, 1917, **18**, 93) and by Vegard (*Z. Physik*, 1921, **5**, 393) alone has shown that they behave as single entity and not as if they were composed of thin laminæ of the individual salts. In the crystal lattice of the mixed crystal, the vicarious elements replace each other atom for atom.

Moreover, in these too, like the liquid solutions many of the physical properties do not necessarily follow the mixture law. For example, it is a well known fact that electrical conductivity of solid solution is much smaller than that of the mechanical mixture of the two metals. Bruni and Meneghini (*Atti. Ist. Veneto*, 1911, ii, 71, 195), M. M. Papov, A. Bundel and V. Choller (*Z. Phys. Chem.*, 1930, 147, 302) have shown that heat of solution of solid solutions of potassium chloride—potassium bromide series is smaller than that of mechanical mixture of the two constituents. Freezing point curves of the solid solutions when plotted may be between the freezing points of the pure components or it may pass through a maximum or a minimum. H. Endo (*Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 479) while studying the relation between the equilibrium diagram and magnetic susceptibility in binary alloys, has shown that though the magnetic susceptibility concentration curve of the mixture of two metals remains straight yet that of a solid solution becomes curved, but no definite relationship between magnetic susceptibility and any other property of solid solution has been arrived at.

In order to determine such a relationship it is necessary that an accurate magnetic study be made of the simpler solid solutions. In the present investigation attention has been restricted to a close examination of the following types of solid solutions.

(1) Those in which the components are simple, stable crystalline salts.

(2) Those which form unbroken series of mixed crystals.

(3) Those which are either truly isomorphous or their freezing point curves pass through a minimum.

Solid solutions of potassium permanganate—potassium perchlorate, potassium chloride—sodium chloride, potassium bromide—potassium chloride and potassiumbromide—sodiumbromide have been examined over the entire range of the composition.

EXPERIMENTAL.

The salts from which these solid solutions were prepared, were the purest obtainable and further purified by fractional crystallisation from water and analysed before use.

Potassium permanganate decomposes on melting. It was necessary, therefore, to make solid solutions of potassium permanganate

and potassium perchlorate by precipitation from aqueous solutions. The method used was that described by Fock (*Z. Kryst.*, 1897, **28**, 337). A solution of the mixture in different proportions in water at a temperature slightly above that of the room, was cooled and vigorously shaken. The crystals that separated were quickly filtered off and dried with filter paper. These were kept in a vacuum desiccator till further use. Since only 2—3 per cent. of the substance in solution crystallised out, the composition of the solid solution can be considered to be constant. The samples got in this way were analysed for potassium permanganate volumetrically and potassium perchlorate when in small quantities by colorimetric method by F. L. Hahn (*Z. angew. Chem.*, 1926, **39**, 451) and when in large quantities by the usual precipitation method.

In other cases as the pure components melt without decomposition, proper amounts of each were weighed, and were ground well in an agate mortar. Portion of the mixture was placed in a hard glass tube which was sealed and was heated in an electric furnace. When the mixture melted, the melt was cooled gradually by lowering the temperature of the furnace and finally kept for 6 hours at about 30-40° below the temperature of solidification. The melt was then quenched to the room temperature, for, otherwise if the molten mixture be cooled slowly after solidification the solid solutions decompose. The quenched mass was kept along with the mechanical mixture in a vacuum desiccator. The percentage composition of the constituents both in the mixture and solid solutions was determined by the usual method and the amounts of the constituents both in the solid solution and the mixture were found to be the same.

The magnetic susceptibility of solid solutions as well as of the mixtures was determined by a magnetic balance of the Wilson type (*Proc. Roy. Soc.*, 1920, **A**, **96**, 429). The substance contained in a small glass tube hooked to an arm of the very light glass system, was suspended in a non-homogeneous magnetic field by a fine quartz fibre. The force exerted by the field was balanced by the torsion of the suspension and read off from a graduated head. The susceptibility of the sample is calculated by the formula of Oxley (*Proc. Roy. Soc.*, 1922, **A**, **101**, 264).

$$x = \frac{1}{M} \left[x_a M_a + (x_u m_u - x_a m_a) \frac{D - D_1}{D_2 - D_1} \right]$$

where x = susceptibility of the specimen,

M = mass of the specimen in grams,

x_a = specific susceptibility of air (210×10^{-7}),

M_a = mass of air filling the same volume as the specimen,

x_w = specific susceptibility of water,

m_w = mass of water filling the same volume as the specimen,

m_a = mass of air filling the same volume as water,

D = torsion due to specimen tube specimen,

D_1 = torsion due to specimen tube alone,

D_2 = torsion due to specimen tube comparison substance (water).

Pure water, which has a mass susceptibility at ordinary temperatures of -7.2×10^{-7} (Wills, *Phys. Rev.*, 1905, 20, 158), was used as the comparison substance in all determinations.

Susceptibility of the pure salts.—The mass susceptibility of the salts from which the solid solutions were prepared are given in Table I, and for comparison the values from International Critical Tables are added.

TABLE I.

Salt.	Mass suscep- tibility $\times 10^7$.	International critical tables $x \times 10^7$.	Kiyoshi Kido $x \times 10^7$.	Bhatnagar. Mathur inter- ference ba- lance, $x \times 10^7$.
Potassium chloride	-5.049	-5.16	-4.81	-5.681
Sodium chloride	-4.888	-4.99	-5.06	-4.902
Potassium bromide	-3.702	-3.77	-4.04	-3.706
Sodium bromide	-3.568	-4.70	-4.20	-3.510
Potassium perchlorate	-2.877	—	—	—
Potassium permanganate	+1.82	+1.80	—	—

The susceptibility of the salts has been determined at various times by different workers and recently by Kiyoshi Kido (*Sci. Rep. Tohoku Imp. Univ.*, 1932, 21, 149). The values differ because the information about the purity and state of hydration of salts is insufficient. The values of these salts, therefore, were checked on the Bhatnagar-Mathur magnetic interference balance set up in this laboratory and the values obtained are given in the last column of Table I.

Potassium perchlorate—potassium permanganate system.—The change of susceptibility with composition of the solid solution and that of mechanical mixture is shown in Fig. 1 and the values are tabulated in Table II.

FIG. 1.
KMnO₄—KClO₄ System.

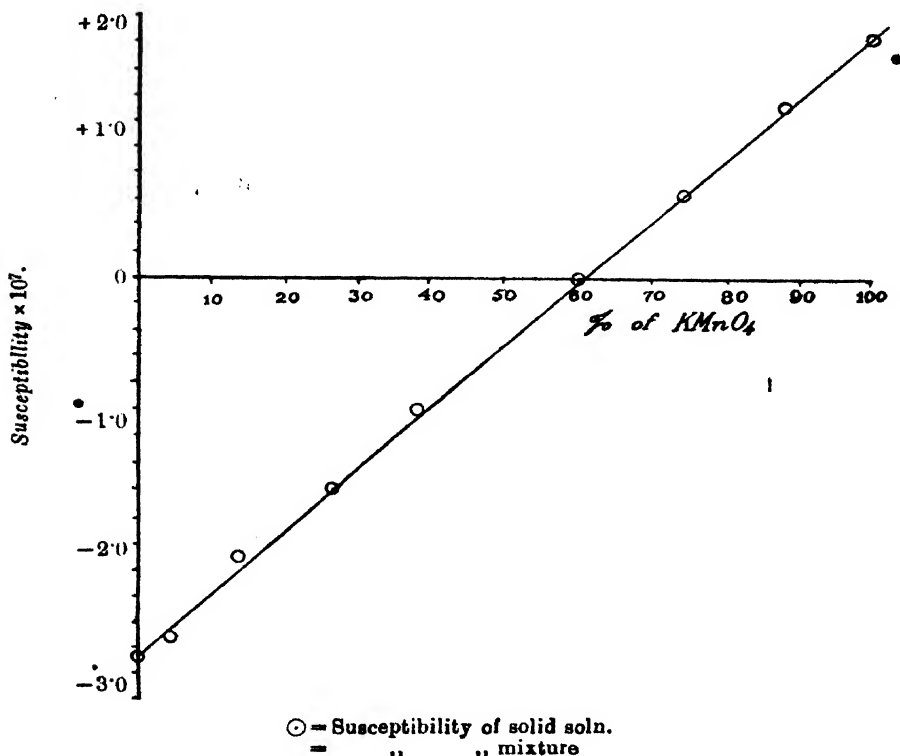


TABLE II.

Mass susceptibility $\times 10^7$.

Specimen.	% of KMnO ₄ .	Mechanical mixture.		Solid solution.
		Calc.	Observed.	
KMnO ₄	100	+1.80	+1.82	...
A	88	+1.256	+1.347	+1.821
B	74	+0.5987	+0.641	+0.622
C	60	-0.0588	No effect	No effect
D	39	-1.0451	-1.012	-0.95
E	27	-1.6088	-1.60	-1.60
F	14.6	-2.1912	-2.157	-2.172
G	5	-2.6421	-2.6401	-2.632
KClO ₄	0	—	-2.877	—

The susceptibility—composition curve for the solid solutions of potassium permanganate—potassium perchlorate follows practically a linear course like that of the mixture. Therefore the susceptibility of potassium perchlorate—potassium permanganate mixed crystals may be calculated approximately by the mixture law from the values of the constituents and the composition of mixed crystals.

Potassium chloride—potassium bromide, sodium chloride—Potassium chloride and potassium bromide—sodium bromide systems.—The susceptibility values for potassium chloride—potassium bromide, sodium chloride—potassium chloride, sodium bromide—potassium bromide solid solutions and those of mixtures are given in Tables III, IV and V. Curves have been plotted for the systems sodium chloride—potassium chloride and sodium bromide—potassium bromide and are shown in Figs. 2 and 3.

FIG. 2.
KCl-NaCl System.

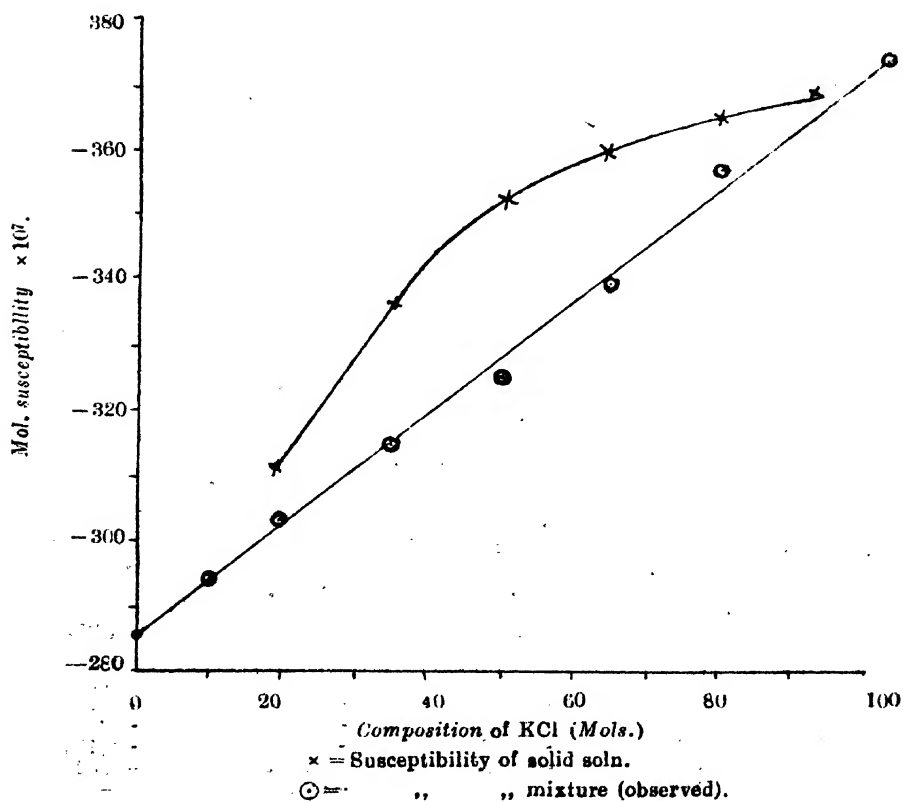


FIG. 3.
NaBr—KBr System.

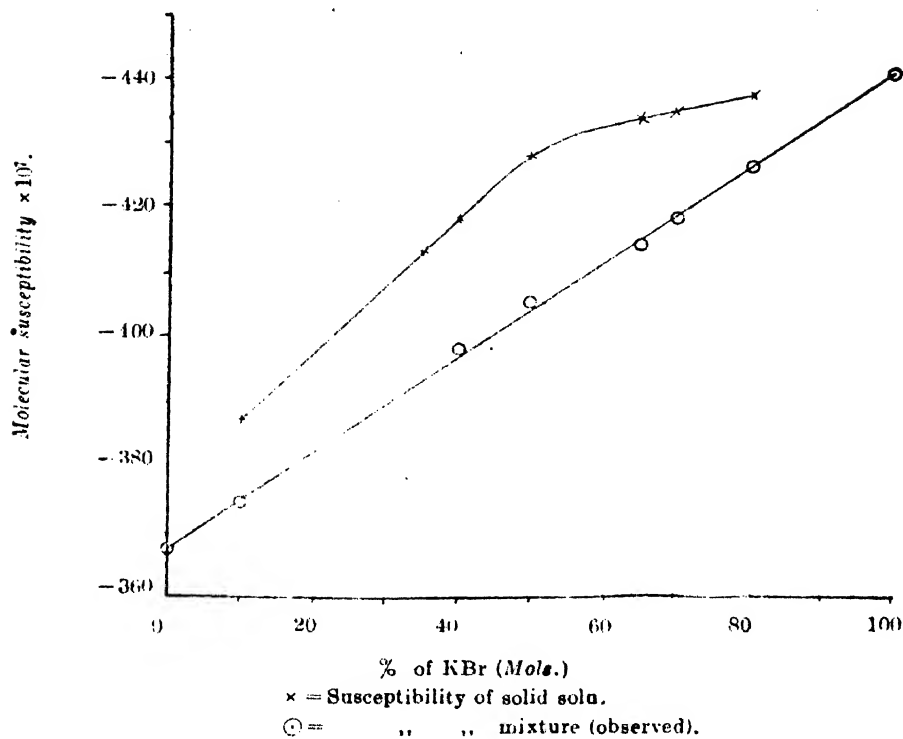


TABLE III.

Potassium chloride—potassium bromide System.

Specimen.	Mol. % KBr	Molecular susceptibility $\times 10^3$			Difference.
		Mechanical Calculated.	mixture. Observed.	Solid solution.	
KBr	100	...	-440.3
A	90	-433.93	-434.2	-434.9	0.7
B	80	-427.56	-428.3	-431.7	3.4
C	70	-421.19	-421.9	-428.3	6.4
D	65	-418.00	-417.7	-422.9	5.2
E	50	-404.0	-408.5	-408.8	0.3
F	35	-397.5	-395.5	-395.7	0.2
G	10	-382.97	-383.0	-388.1	0.1
KCl	0		-376.6		

TABLE IV.

Potassium Chloride—Sodium Chloride System.

Specimen.	Mol. % KCl	Molecular susceptibility $\times 10^7$		Solid solution.	Difference.
		Mechanical mixture.			
		Calculated.	Observed.		
KCl	100	...	-376.6
A	93	-370.2	-369.4	-370.1	0.7
B	80	-358.4	-357.5	-365.7	8.2
C	65	-344.71	-339.4	-360.0	20.6
D	50	-331.3	-325.4	-352.0	26.6
E	35	-316.8	-315.9	-338.6	22.7
F	20	-304.12	-303.5	-310.1	6.6
G	10	-295.06	-294.4
NaCl	0	...	-286.6

TABLE V.

Potassium bromide—Sodium Bromide System.

Specimen _z	Mol. % of KBr.	Molecular susceptibility $\times 10^7$		Solid solution.	Difference.
		Mechanical mixture			
		Calculated.	Observed.		
KBr.	100		-440.3		
A	80	-425.66	-426.0	-437.2	11.20
B	70	-418.34	-418.2	-434.1	15.9
C	65	-414.68	-414.7	-432.0	17.3
D	50	-403.70	-407.0	-427.7	27.7
E	40	-396.90	-398.5	-417.5	19.0
F	35	-394.50	-396.0	-414.2	18.2
G	10	-374.42	-376.0	-388.7	12.2
NaBr	0		-367.1		

The susceptibility-composition curve of the solid solutions in case of potassium chloride—sodium chloride and potassium bromide—sodium bromide passes through a maximum and the maximum in both the cases is at 50% composition. The curve in the case of potassium chloride—potassium bromide is very slightly curved with a maximum at 70% composition potassium bromide.

Results.

From the results given in Tables I to V, we can arrive at the following conclusions: (1) the susceptibility-concentration curve of a system of solid solution may follow a linear course, or (2) it may pass through a maximum.

In potassium perchlorate—potassium permanganate system, which is a true isomorphous system, the susceptibility-concentration curve is practically a straight line. This is what is expected because the truly isomorphous substances are those in which the physical properties are continuous functions of the percentage composition of the constituents (Retger's law) and the magnetic susceptibility would thus naturally be expected to follow the Retger's law.

In potassium chloride—potassium bromide, sodium chloride—potassium chloride and sodium bromide—potassium bromide systems, it is found that the susceptibility concentration curve passes through a maximum. The maximum in the system potassium chloride—potassium bromide is at 70 per cent. molecular composition of potassium bromide and in the systems sodium chloride—potassium chloride, sodium bromide—potassium bromide, the maximum lies at 50 per cent.

If the freezing point curves for potassium chloride—potassium bromide (Amadori U. Pampanini: *Rend. Linc.*, 1911, (5), 20, ii, 572) potassium chloride—sodium chloride and potassium bromide—sodium bromide (Kurankow and Zemczuznyj, *Z. anorg. Chem.*, 1907, 52, 186), systems be studied, they can be classed among that type of solid solutions in which the freezing point curve passes through a minimum, and that point in potassium chloride—potassium bromide system is at 70 per cent. molecular composition of potassium bromide and in sodium chloride—potassium chloride, potassium bromide—sodium bromide systems is at 50 p.c. molecular composition. Thus we observe that the solid solutions having percentage composition for which the melting point is a minimum, has the maximum magnetic susceptibility for that very composition. This fact is not true in case of salt solutions only but is also true of metallic solutions like that of copper-gold where we find that magnetic susceptibility-concentration curve has a maximum whereas the freezing point curve passes through a minimum.

This suggests a possible correlation of the heat of formation of different systems with the magnetic susceptibilities of the systems. For example, Table VI shows the heat of formation and the susceptibility of solid solution of that percentage composition which has a maximum value.

TABLE VI.

System.	Molecular per cent. composition.	Susceptibility curve.	Heat of formation.	Reference.
KClO ₄ -KMnO ₄	...	Linear	0 Cals.	Sommerfeld ¹
KCl-KBr	70 % KBr	Curved	220	Bruni and Amadori; ² M.M. Popov, A. Buedel and V. Choller. ³
KBr-NaBr :	50 % KBr	Curved	1400	Kurnakow and Zemczuczni ⁴
KCl-NaCl	50 % KCl	Curved	2100	do

From the results tabulated above, it is clear that the greater heat of formation of the solid solution is synonymous with the greater magnetic susceptibility of the system. When the heat of formation of the system is zero, the susceptibility-concentration curve of that system follows a linear course.

¹. *Z. Phys. Chem.*, 1901, **36**, 754.

². *Atti. ist. Veneto.*, 1911, ii. **71**, 51.

³. *Z. Phys. Chem.*, Ab. A., 1930, **147**, 302.

⁴. *Z. anorg. Chem.*, 1907, **52**, 186,

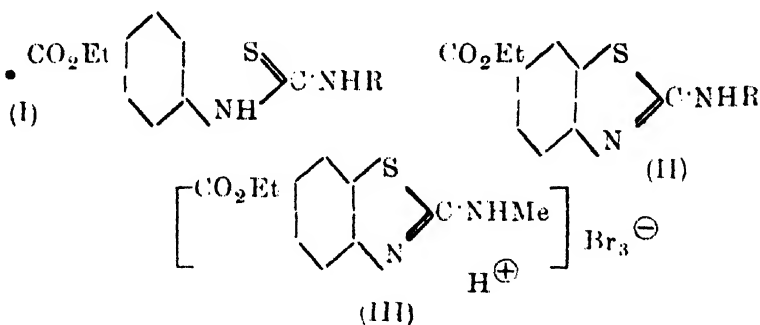
Revised. July 7, 1932.

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The Interaction of *s-p*-Carbethoxyphenylalkylthiocarbamides with Bromine and a Note on the Effect of the *iso*Butyl group on Hydrotribromide Formation in 1-Alkylaminobenzthiazoles.

BY ROBERT FERGUS HUNTER AND EDWIN RICHARD PARKEN.

In the course of an investigation on the effect of *meta*-directive substituents on the mobility of semi-cyclic amidines (*cf.* Hunter and Jones, *J. Chem. Soc.*, 1930, 2190), it appeared of interest to examine the bromination of certain *s-p*-carbethoxyphenylalkylthiocarbamides (I) in relation to the capacity of the corresponding alkylaminobenzthiazoles (II) for polybromide ion formation.



On treatment with bromine in chloroform under conditions in which arylthiocarbamides normally undergo thiazole cyclisation with elimination of hydrogen bromide, *s-p*-carbethoxyphenylmethylthiocarbamide (I, R=Me) gave rise to a well-defined hydrotribromide of ethyl-1-methylaminobenzthiazole-5-carboxylate (III), which yielded the aminobenzthiazole (II, R=Me) on reduction with sulphurous acid in the usual way (Hunter, *J. Chem. Soc.*, 1925, 127, 2023, 2270; 1926, 1385, and later). Unlike the hydroperebromides of 1-amino-5-methylbenzthiazole (Hunter, *loc. cit.*), 1-methylamino 5-methylbenzthiazole (Hunter and Jones, *loc. cit.*), and 5-chloro-1-methylaminobenzthiazole (Dyson, Hunter, Jones, and Styles, *J. Indian. Chem. Soc.*, 1931, 8, 148), however, this bromo-addition compound did not undergo nuclear substitution in aqueous alcoholic solution.

It might have been anticipated on *a priori* grounds that the presence of the *meta*-directive carbethoxy group in the 5-position of the benzthiazole system would cause substitution at the carbon atom (3), and this therefore provides a further example of the fact that *meta*-directive grounds do not really favour *meta* substitution, but rather that they favour *o-p*-substitution less. This is of course embodied in the general conception (Ingold, *Annual Reports of the Chemical Society*, 1926, 134) that *meta* substitution is a residual effect produced by the disappearance of free affinity from the *o-p*-positions.

Both *s-p*-carbethoxyphenylethylthiocarbamide and *s-p*-carbethoxyphenylisobutylthiocarbamide (I, R=Et, and *iso*-C₄H₉ respectively) behaved similarly to the methylthiocarbamide, and yielded well defined hydrotribromides of the corresponding alkylaminobenzthiazoles on bromination under the usual conditions.

The *s-p*-carbethoxyphenylalkylthiocarbamides therefore differ from other *p*-substituted phenylalkylthiocarbamides in that the bromination of both the methyl and the isobutyl derivatives gives rise to hydrotribromides (*cf.* Dyson, Hunter, Jones and Styles, *loc. cit.*).

The effect of the isobutyl group in promoting hydrotribromide formation in 1-alkylaminobenzthiazoles appears noteworthy since *s*-phenylisobutylthiocarbamide itself gives rise to the hydrotribromide of 1-isobutylaminobenzthiazole on bromination in chloroform (Hunter, *J. Chem. Soc.*, 1926, 2951). Moreover, a reinvestigation of the bromination of *s-p*-bromophenylalkylthiocarbamides (Hunter and Soyka, *J. Chem. Soc.*, 1926, 2958) which will be published in the near future, has shown that the careful bromination of *s-p*-bromophenylisobutylthiocarbamide gives rise to an unstable hydrotribromide of 5-bromo-1-isobutylaminobenzthiazole which undergoes dissociation into the stable "dibromide" described in 1926, and bromine.

EXPERIMENTAL.

The thiocarbonyl chloride used in these experiments was prepared from carbon disulphide by way of thiocarbonyl perchloride, which was obtained by passing chlorine from a cylinder through a solution of 1 g. of iodine in 1000 c. c. of carbon disulphide in the apparatus already described (Dyson and Hunter, *J. Soc. Chem. Ind.*, 1926, 45, 81r), until a gain in weight of 25 p. c. was observed. The sulphur chloride was decomposed by steam in the usual way, and the thiocarbonyl perchloride isolated by distillation.

Attempts to replace granulated tin and hydrochloric acid by zinc and hydrochloric acid in the reduction of the perchloride again proved unsuccessful. This is doubtless due to the fact that the former reagent carries the reduction beyond the thiophosgene stage. The yield of thiocarbonyl chloride obtained in this way, after redistillation was usually of the order of 25 p. c.; b. p. 72-75°/760 mm.

p-Carbethoxyphenylthiocarbimide was prepared by gradually adding a solution of ethyl-*p*-aminobenzoate (1 mol.) in chloroform, to a well stirred suspension of thiocarbonyl chloride (1.3 mols.) in water (10 vols.) at 15-20°. The chloroform layer was then separated and the excess of thiocarbonyl chloride distilled off along with the solvent from a water-bath, and the product recrystallised from dilute alcohol. The thiocarbimide formed very pale yellow glistening plates with the odour of aniseed, m. p. 58°, yield 70-80 p. c.

s-p Carbethoxyphenylmethylthiocarbamide.—5 G. of *p* carbethoxyphenylthiocarbimide in alcohol (30 c. c.) were treated with 30 p. c. excess of a solution (33 p. c.) of methylamine in the same solvent, and the mixture was kept for a short time and then boiled for a few minutes. The solution was cooled and kept for 3 hours and the product recrystallised from absolute alcohol when the thiocarbamide formed aggregates of needles, m. p. 147-48°, yield 80-90 p. c. (Found: S, 13.6. $C_{11}H_{14}O_2N_2S$ requires S, 13.4 per cent.).

Ethyl-1-methylaminobenzthiazole-5-carboxylate hydrotribromide.—1 G. of *s-p*-carbethoxyphenylmethylthiocarbamide in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent), and the mixture was heated on a water-bath under reflux for 10 minutes, when hydrogen bromide was freely evolved. The solution was transferred to a glass basin and concentrated under reduced pressure at laboratory temperature, when a red gum was obtained which crystallised on scratching with a glass rod. The hydrotribromide formed small orange crystals which were crushed on porous earthenware and dried in a vacuum over potassium hydroxide and calcium chloride, m.p. 137-38° (decomp.). [Found: Br (total), 50.8; Br (labile), 34.0. $C_{11}H_{12}O_2N_2S$, HBr(Br₂) requires Br (total), 50.3; Br (labile), 33.5 per cent.]. The hydrotribromide dissolved in alcohol giving a yellow solution, which evolved aldehyde after being diluted with water and boiled. On concentration this yielded a hydrobromide, which on basification with ammonia gave ethyl-1-methylaminobenzthiazole-5-carboxylate, identical with that obtained by reduction of the hydrotribromide with sulphurous acid.

Ethyl-1-methylaminobenenthiazole-5-carboxylate.—The hydrotribromide (1 g.) was suspended in sulphurous acid (100 c.c.) and sulphur dioxide was passed through the mixture until a clear solution was obtained. On basification with ammonia ethyl-1-methylaminobenenthiazole was obtained, which separated from alcohol-ethyl acetate in glistening plates, m.p. 169°. (Found: S, 18.6. $C_{11}H_{12}O_2N_2S$ requires S, 18.6 per cent.). The acetyl derivative, obtained by heating a solution of the base in acetic anhydride for a few minutes and diluting with alcohol, separated from methyl alcohol in white prisms, m.p. 174°. (Found: S, 11.6. $C_{13}H_{14}O_4N_2S$ requires S, 11.5 per cent.).

1-Methylaminobenenthiazole-5-carboxylate.—A solution of ethyl-1-methylaminobenenthiazole-5-carboxylate in concentrated hydrochloric acid was heated under reflux on a sand-bath for 40 minutes, when the sparingly soluble acid separated as a fine precipitate which was collected and recrystallised from a large volume of boiling alcohol-ethyl acetate. The carboxylic acid formed small fine white crystals, which were readily soluble in alkalis, and which were unmelted at 298°. (Found: S, 16.1. $C_9H_8O_2N_2S$ requires S, 15.4 per cent.).

s-p-Carbethoxyphenylethylthiocarbamide.—The solution obtained from *p*-carbethoxyphenylthiocarbimide (3 g.), absolute alcohol (15 c.c.) and 8.5 c.c. of a 33 p. c. solution of ethylamine in water did not crystallise after being heated to boiling point and kept for 3 hours. On concentration and recrystallisation from absolute alcohol, the *ethylthiocarbamide* was obtained in small glistening needles, m.p. 89°. (Found: S, 12.4. $C_{12}H_{16}O_2N_2S$ requires S, 12.7 per cent.).

Ethyl-1-ethylaminobenenthiazole-5-carboxylate hydrotribromide.—*s-p*-Carbethoxyphenylethylthiocarbamide (0.9 g.) in chloroform (8 c.c.) was treated with bromine (0.9 c.c. in 1 c.c. of chloroform) and the mixture was heated for 10 minutes under reflux. The red solution was concentrated in a vacuum until crystallisation took place. The *hydrotribromide* formed small orange red crystals which had m.p. 108.04° (decomp.) after drying. [Found: Br (total), 48.8; Br (labile), 31.7. $C_{12}H_{14}O_2N_2S$, HBr (Br_2) requires Br (total), 48.9; Br (labile), 32.6 per cent.].

Ethyl-1-ethylaminobenenthiazole-5-carboxylate.—The hydrotribromide was added to a large volume of sulphurous acid and sulphur dioxide was passed through the mixture until reduction was complete. On basification of the filtered solution with ammonia, the base was

obtained, which crystallised from methyl alcohol in small glistening plates, m.p. 150-51°. (Found: S, 15·1. $C_{12}H_{14}O_2N_2S$ requires S, 15·0 per cent.).

s-p-Carbethoxyphenylisobutylthiocarbamide.—The thiocarbimide (2 g.) in absolute alcohol (10 c.c.) was treated with a 33 p. c. solution of isobutylamine in water (2·5 c.c.) and the solution was boiled and cooled. The isobutylthiocarbamide separated from alcohol in glistening needles, m.p. 107-08°. (Found: S, 11·6. $C_{14}H_{20}O_2N_2S$ requires S, 11·4 per cent.).

Ethyl-1-isobutylaminobenzthiazole-5-carboxylate hydrotribromide.—A solution of the carbethoxyphenylisobutylthiocarbamide (1·5 g.) in chloroform (6 c.c.) was treated with bromine (1·5 c.c. diluted with 1 c.c. of chloroform) and the solution was heated under reflux for 10 minutes, cooled, and concentrated under reduced pressure at laboratory temperature. The hydrotribromide crystallised on keeping in an evacuated desiccator over potassium hydroxide, for some hours and scratching with a glass rod, and formed orange crystals, m.p. 92-94° (softening at 90°) after being dried in the usual way. [Found: Br (total), 47·16; Br (labile), 29·6. $C_{14}H_{18}O_2N_2S$, $HBr(Br_2)$ requires Br (total), 46·3; Br (labile), 28·9 per cent.].

Ethyl-1-isobutylaminobenzthiazole-5-carboxylate was obtained by reduction of the hydrotribromide with sulphurous acid and sulphur dioxide as in the previous case, and separated from methyl alcohol in small glistening crystals, m.p. 133-34°. (Found: S, 11·4. $C_{14}H_{18}O_2N_2S$ requires S, 11·5 per cent.).

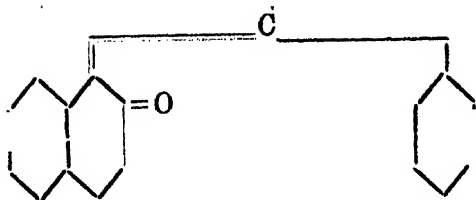
THE TECHNICAL COLLEGE,
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ALIGARE.

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ERRATA

Page	Line				
97	22	for $\equiv 0.0000375g.$	read $\equiv 0.0009375g.$
• 173	14	fn	of
177	3	filter	filtrate
177	5		"described" before
					"by"
181	3	benzylol	benzoyl
181				read the last formula as	

OH



Rotatory Powers of some Substituted Camphoranilic Acids and Camphorophenyl Imides.

BY MAHAN SINGH AND RATTAN CHAND BHALLA.

It has been stated by Rule (*J. Chem. Soc.*, 1924, 125, 1127), that groups of like polarity reinforce each other in the *ortho*-position whilst the introduction of a positive and a negative group both of marked polarity leaves the rotation of unsubstituted compounds unaltered. This is supported by the case of the menthyl esters of *o*-disubstituted benzoic acid prepared by Cohen (*J. Chem. Soc.*, 1914, 105, 1892). Singh and Singh (*J. Chem. Soc.*, 1931, 478) have prepared some disubstituted camphoranilic acids and have determined their rotatory powers in various solvents. They have shown that groups of the same polarity reinforce each other when they are in the *para*-position with respect to one another; for instance 2':5'-dimethylcamphoranilic acid and 5'-nitro-2'-methylcamphoranilic acid exceed any of their respective isomerides in rotatory power. Again groups of opposite polarity neutralise each other's effect when present in *para*-position. The rotatory power of 5'-nitro-2'-methoxycamphoranilic acid is practically the same as that of the unsubstituted compound (*loc. cit.*). The work has been extended to other disubstituted camphoranilic acids and camphoro—disubstituted phenylimides. The following acids and their imides have been prepared: 2':4'- and 3':5'-dimethyl-, 2':4'-dichloro-, 2':5'-methoxy-, 3'-methoxy- and 3'-ethoxycamphoranilic acids. The nitration of 2'- and 3'-methylcamphoranilic acids and 2'-methoxy- and 2'-ethoxycamphoranilic acids has been carried out by the method described in the experimental part. 2'-Methylcamphoranilic acid on nitration gives 4'-nitro-2'-methylcamphoranilic acid as this substance is identical with the condensation product of camphoric anhydride with *m*-nitro-*o*-toluidine, $C_6H_3CH_3 \cdot NH_2 \cdot NO_2$ (1:2:5). The two compounds have practically the same rotatory power (*vide infra* and *J. Chem. Soc.*, 1931, 480). Similarly 2'-methoxycamphoranilic acid on nitration gives 4'-nitro-2'-methoxycamphoranilic acid. Both have feeble rotatory power in all the four solvents

examined (*vide infra* and *loc.cit.*). The following table records the rotatory powers of some camphoranilic acids and the nitro derivatives of a few.

TABLE I.

Substituents.	[M] _D			
	MeOH.	EtOH.	Me ₂ OH.	MeEtCO.
2'-OH ₃ 146	144	98	...
3'-CH ₃ 140	118	89	...
4'-CH ₃ 167	144	120	...
2':4'-Dimethyl 163	160.9	117	107
3':5'-Dimethyl 135	126	83.6	84
2'-CH ₃ -4'-Nitro 92	90	...	74
3'-CH ₃ -2'-Nitro -14.9	-25	-26	-17
2'-OCH ₃ 30	28	-16	-10
2'-OCH ₃ -4'-Nitro	Feeble rotation in all solvents.		
2'-OC ₂ O ₅ -50	-62	-90	-89
2'-OC ₂ O ₅ -4'-Nitro -48	-41.8	-32	-31

A glance at the table will show that the optical rotatory power of 3':5'-dimethylcamphoranilic acid is practically the same as that of the 3'-methylcamphoranilic acid. Again 2':4'-dimethylcamphoranilic acid has practically the same rotation as that of the 4'-methylcamphoranilic acid except in the case of ethyl alcohol where there is a slight increase. The substitution of another CH₃ group in the *meta*-position does not therefore bring about any change.

Nitro group in the 4'-position has a depressing effect upon the rotatory power of the original compound. Thus 2'-methyl-4'-nitro-, 2'-methoxy-4'-nitro-, and 2'-ethoxy-4'-nitro- have all lower values than the original compounds.

The nitro group in the 2'-position in the case of 3'-methyl-2'-nitrocamphoranilic acid lowers the rotation accompanied by a reversal of sign but the effect is not so marked as in the case of 4'-methyl-2'-nitrocamphoranilic acid (*J. Chem. Soc.*, 1931, 480) where the groups are present in the *meta*-position with respect to one another.

Table II records the molecular rotatory powers of 2'-methoxy-, 3'-methoxy-, and 2':5'-methoxycamphoranilic acids.

TABLE II.

Solvent.	$[M]_D$		
	2'-OCH ₃ .	3'-OCH ₃ .	2':5'-OCH ₃ .
MeOH	30	151.6 (110)	91.7
EtOH	28	127.5 (131)	67.3
Me ₂ CO	-16	99.7 (101)	43.0
MeEtCO	-10	96.7 (-)	44.0

3'-Methoxycamphoranilic acid has the same values of rotatory power as the unsubstituted compound. (The values of the rotatory power of the latter are shown in parentheses in Table II). The OCH₃ group in the 2'-position lowers the values but the effect is not so marked in 2':5'-dimethoxy-, as in the case of the 2'-methoxycamphoranilic acid.

The following table gives the values of 2'-chloro-, 4'-chloro-, and 2':4'-dichlorocamphoranilic acids in four solvents.

TABLE III.

Solvent.	$[M]_D$		
	2'-Chloro.	4'-Chloro.	2':4'-Chloro.
MeOH	57.8	163.0	86.6
EtOH	35.6	158.7	87.4
Me ₂ CO	-40.8	119.0	feeble positive
MeEtCO	-26.6	150.3	do

The chlorine atom in 2'-position has a depressing effect on the rotatory power of the original compound.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Substituted Amines.

Camphoric anhydride and the amine (equal mols.) were heated together with fused sodium acetate at 140-45° for 3-4 hours. The product was dissolved in 90 p.c. alcohol, precipitated, extracted with

a dilute solution of alkali to remove any imide, acidified, and crystallised from alcohol. The following acids were prepared :

3':5'-Dimethylcamphoranilic acid crystallised from alcohol in silky needles, m.p. 214-15°. (Found: N, 4.63; Eq. wt., 304. $C_{18}H_{25}O_3N$ requires N, 4.6 per cent. Eq. wt., 303).

The imide is also formed to the extent of about 10 per cent.

2':4'-Dimethylcamphoranilic acid was obtained as a crystalline mass, m.p. 220-21°. (Found: N, 4.64; Eq. wt., 304.7. $C_{18}H_{25}O_3N$ requires N, 4.6 per cent. Eq. wt., 303).

2':4'-Dichlorocamphoranilic acid crystallised from dilute alcohol in white crystals, m.p. 200-01°, yield 30 p.c. (Found: N, 3.2; Eq. wt., 341.5. $C_{16}H_{19}O_3NCl_2$ requires N, 3.15 per cent. Eq. wt., 344). The acid is soluble in the usual organic solvents.

2':5'-Dimethoxycamphoranilic acid crystallised from alcohol in fine needles with a pink tinge, m.p. 137-39°, yield of the acid is almost quantitative. (Found: N, 4.24; Eq. wt., 331. $C_{18}H_{25}O_5N$ requires N, 4.18 per cent. Eq. wt., 335).

3'-Methoxycamphoranilic acid crystallised from 50 p.c. alcohol in white needles, m.p. 186.5°, yield 75 p.c. (approx.). (Found: N, 4.63; Eq. wt., 305.3. $C_{17}H_{23}O_4N$ requires N, 4.57 per cent. Eq. wt., 305).

3'-Ethoxycamphoranilic acid crystallised from dilute alcohol in white needles, m.p. 168°, yield 80 p.c. (approx.). (Found: N, 4.48; Eq. wt., 319. $C_{18}H_{25}O_4N$ requires N, 4.38 per cent. Eq. wt., 319).

Camphoric anhydride could not be condensed with 2:5-dichloroaniline.

Camphoro-2':4'-dichlorophenyl imide crystallised from dilute alcohol to colourless crystals, m.p. 62.5°, yield 20 p.c. (approx.). (Found: N, 4.35. $C_{16}H_{17}ONCl_2$ requires N, 4.29 per cent.).

Camphoro-2':5'-dimethoxyphenyl imide crystallised from dilute alcohol in colourless crystals, m.p. 111-12°, yield 75 p.c. (approx.) (acid, m.p. 137-39°). (Found: N, 4.5. $C_{18}H_{23}O_4N$ requires N, 4.41 per cent.).

Camphoro-m-methoxyphenyl imide crystallised from alcohol in colourless crystals, m.p. 121-23°, yield 75 p.c. (approx.). (Found: N, 5.0. $C_{17}H_{21}O_3N$ requires N, 4.88 per cent.).

Camphoro-m-ethoxyphenyl imide crystallised from dilute alcohol in colourless crystalline mass, m.p. 93-95°. The yield is comparatively less in this case, 50 p.c. (Found: N, 4.89. $C_{18}H_{23}O_3N$ requires N, 4.65 per cent.).

Camphoro-2':6'-dimethylphenyl imide crystallised from dilute alcohol in a crystalline colourless product, m.p. 154-55°. (acid, m.p. 236-38°), yield 80 p.c. (approx.). (Found: N, 5.0. $C_{18}H_{23}O_2N$ requires N, 4.91 per cent.).

Nitration of Camphoranilic Acids.

To a mixture of fuming nitric acid (10 c.c.) and glacial acetic acid (8 c.c.) 3 g. of the compound were gradually added. The clear solution obtained after 5-10 minutes was kept $\frac{1}{2}$ hour and then poured on crushed ice. The precipitate obtained was crystallised from alcohol.

2'-Methoxy-4'-nitrocamphoranilic acid.—The reaction mixture was added drop by drop into ice-cold water, otherwise a large amount of resinous matter was obtained. Crystallised from dilute alcohol in pale yellow crystals, m.p. 182-84°. (Found: N, 8.28. $C_{17}H_{22}O_6N_2$ requires N, 8.0 per cent.).

This compound is identical with the condensation product of camphoric anhydride with *m*-nitro-*o*-anisidine $C_6H_3(OCH_3)(NH_2)NO_2$ (1:2:5) prepared by Singh and Singh (*loc. cit.*). They give the melting point 185-86°. Both have feeble rotations, the former having $[\alpha]_D$, 5.7 and the latter $[\alpha]_D$, 5.0 in methylethyl ketone.

2'-Ethoxy-4'-nitrocamphoric acid.—This was similarly poured into cold water and crystallised in yellow coloured bars from dilute alcohol, m.p. 171-73°. (Found: N, 8.0. $C_{18}H_{24}O_6N_2$ requires N, 7.7 per cent.).

2'-Methyl-4'-nitrocamphoranilic acid.—The reaction mixture on being poured into ice, separated as a resinous matter which on crystallisation from dilute alcohol gave brownish yellow needles, m.p. 226-28°. (Found: N, 8.5. $C_{17}H_{22}O_5N_2$ requires N, 8.38 per cent.).

The nitration product of 2'-methylcamphoranilic acid is identical with 2'-methyl-4'-nitrocamphoranilic acid obtained by Singh and Singh by condensing camphoric anhydride with *m*-nitro-*o*-toluidine (*loc. cit.*). They give the m.p. 229-30°, and the following values for rotatory powers $[\alpha]_D$, in methyl alcohol, 29.1°; ethyl alcohol, 24°; and methylethyl ketone, 23°. The values of the substance prepared by the authors for the same solvents are 27.6°, 27° and 22.4°.

3'-Methyl-2' (or 6')-nitrocamphoranilic acid.—The reaction product was poured into ice. It was crystallised from dilute alcohol in yellow

crystals, m.p. 139-40°. (Found: N, 8.4. $C_{17}H_{22}O_5N_2$ requires N, 8.38 per cent.).

Rotatory Powers of Mono- and Disubstituted Camphoranilic Acids and Imides.

TABLE IV.

Solvent.	2' : 4'-Dimethylcamphor- anilic acid.		3' : 5'-Dimethylcamphor- anilic acid.		2'-Methyl-4'-nitro- camphoranilic acid.	
	Conc. g/25c.c.	$[M]_D$	Conc. g/25c.c.	$[M]_D$	Conc. g/25c.c.	$[M]_D$
MeOH	0.1780	163°	0.2034	135.7°	0.1178	92.0°
EtOH	0.1813	160.9	0.2248	126.3	0.1482	90.1
Me ₂ CO	0.1784	117.5	0.1989	83.6	—	—
MeEtCO	0.2196	107.0	0.1574	84.2	0.1784	74.2°
	3'-Methyl 6'-nitro- camphoranilic acid.		2'-Methoxy-4'-nitro- camphoranilic acid.		2'-Ethoxy-4'-ni camphoranilic a _o	
MeOH	0.1670	-14.99	Shows feeble rotatory power in all the solvents.		0.2532	-48.1 ^{id.}
EtOH	0.1492	-25.18			0.3261	-41.4 ⁸
Me ₂ CO	0.1920	-26.12			0.4125	-31.1 ⁸⁶
MeEtCO	0.1858	-17.26			0.3672	-30.9 ⁹⁹
	2' : 5'-Dimethoxy- camphoranilic acid.		2' : 4'-Dichloro- camphoranilic acid.		3'-Methoxy- camphoranilic acid.	
MeOH	0.3215	91.74	0.1932	86.6	0.2675	151.6
EtOH	0.3488	67.3	0.1572	87.4	0.2238	127.5
Me ₂ CO	0.3015	43.0	Feeble rotations.		0.2291	99.7
MeEtCO	0.2160	44.0			0.2169	99.7
	-Ethoxycamphor- anilic acid.		Camphoro-2' : 5'-dimethoxy- phenyl imide.		Camphoro-3'-methoxy- phenyl imide.	
MeOH	0.2096	159.5	0.2040	34.9	0.2306	38.75
EtOH	0.2205	147.0	0.2186	29.5	0.1937	42.48
Me ₂ CO	0.2055	104.7	—	—	0.2156	39.90
MeEtCO	0.2487	109.0	—	—	0.2198	37.5

TABLE IV. (*Contd.*)

Solvent.	Camphoro-3'-ethoxy- phenyl imide.		Camphoro-2' : 6'-dimethyl phenyl imide	
MeOH	0.2040	62.6	0.2137	46.8
EtOH	0.2126	58.3	0.2175	45.8
Me ₂ CO	0.1912	43.1	0.2152	37.9
MeEtCO	0.1550	38.84	0.2184	39.0

The readings were taken in a 2 dm. tube within half hour of making up the solution. There was no mutarotation. Temperature of the room was 19-20°.

Summary.

A number of new monosubstituted and disubstituted camphor-anilic acids have been prepared and their rotatory powers determined. It has been shown that a second CH₃ group in the *meta*-position does not alter the rotation of the original compound. Further nitro group in the 4'-position has a depressing effect on the rotatory power. Thus 2'-methyl-4'-nitrocamphoranilic acid, 2'-methoxy-4'-nitrocamphoranilic acid and 2'-ethoxy-4'-nitrocamphoranilic acid have lower rotatory power than the original compound.

Methoxy and chloro groups in the 2'-position have also depressing influence, as shown by the rotatory powers of 2' : 5'-dimethoxy- and 2' : 4'-dichlorocamphoranilic acids.

Studies in Organo-arsenic Compounds. Part I.

BY HIRENDRA NATH DAS-GUPTA.

The physiological activity of azo and bisazo compounds have been shown to be dependent on the following factors: (1) presence of $-N=N-$, (2) the capability of liberating salicylic acid or its simple derivative due to decomposition, *e.g.*, Era chrome black or Chrysamin, (3) presence of naphthalene nucleus which hastens the formation of skin, *e.g.*, Biebrich scarlets, Scarlet R, etc., and (4) for trypanocidal activity, the terminals joining the azo groupings must contain naphthalene nucleus with sulphonic and amino groups (Nicolle and Mesnil, *Ann. Inst. Pasteur.*, 1906, **20**, 417).

It has also been found that the media in which the coupling takes place, play an important rôle so far as the trypanocidal activity is concerned. Thus the compounds obtained by coupling in acid medium, have very little or no action upon trypanosomes and if, however, the coupling is performed in alkaline solution, entirely different products are obtained leading almost invariably to the complete disappearance of the said bacillus.

The compounds containing naphthalene ring described in this paper, although they do not contain amino group, are expected to have enhanced trypanocidal activity due to the presence of arsenic in place of amino group. The coupling was done in alkaline media. The following are the additional considerations that may be put forward in favour of the new series of compounds. Modern researches on the diseases due to the parasitic organism, have pointed out clearly the reason why large number of synthetic drugs, very active from theoretical considerations, failed to bring about the expected result. The reason, assigned to the failure of such cases, is that these classes of compounds cannot penetrate into the actual seat of the organism on account of the absence of lipolytic action. The compounds described in the paper, are expected to have the lypolytic properties due to the presence of naphthyl sulphonic acid residue (Twitchell's reagent).

The compounds had all been prepared by diazotising the different aminocoumarins and coupling them in alkaline media with naph-

thylsulphoarsinic acid. This latter compound was prepared by Hill and Balls (*J. Amer. Chem. Soc.*, 1922, **44**, 2051) by sulphonating naphthylarsinic acid, but the authors did not undertake to find out the exact position to which the sulphonic acid group entered the nucleus. Hence the nomenclature used throughout was a general one, without assigning any restricted position to any group.

The compounds which are all yellow dissolve in alkali with a deep red colour and are precipitated by acids. The compounds were crystallised from glacial acetic acid.

EXPERIMENTAL.

Coumarin-6-azonaphthylsulphoarsinic acid.— Naphthylsulphoarsinic acid (4 g.) was dissolved by stirring in 25 p.c. solution of sodium hydroxide. To this a few c.c. more of sodium hydroxide was added and was allowed to cool to 0° in an ice-bath. 6-Aminocoumarin (2 g.) was dissolved in a solution of hydrochloric acid (1 c.c. in 8 c.c. water). The solution was heated and then filtered hot to free it from insoluble matters. The filtrate was cooled to 0° and to this powdered ice was added. The well-cooled solution was next diazotised with a solution of sodium nitrite (0.4 g. in 5 c.c. water). The resulting diazo solution was added with constant stirring to the alkaline solution of the sulphoarsinic acid kept at 0°. The whole was allowed to stand overnight and then filtered. The red solution was acidified with hydrochloric acid, which gave a yellow precipitate. This was separated, dried and then recrystallised from acetic acid in a yellow microcrystalline product, m.p. 185° (decomp.). The acid is insoluble in water but dissolves readily in caustic alkalis and alkaline carbonates. (Found: N, 5.45; As, 14.76. $C_{19}H_{13}O_8N_2SA_s$ requires N, 5.55; As, 14.88 per cent.).

7-Methylcoumarin-6-azonaphthylsulphoarsinic acid.— This was prepared in a similar way from 7-methyl-6-aminocoumarin as the previous one. The only precaution that was necessary was that the acid solution of the amino compound was treated with excess of pounded ice and the nitrite solution was added all at once. The compound was precipitated as a dark brown mass as before with hydrochloric acid and was recrystallised from acetic acid in yellow powder. It shrinks at 169° and decomposes at 235°. (Found: N, 5.30; As, 14.2. $C_{20}H_{15}O_8N_2SA_s$ requires N, 5.4; As, 14.4 per cent.).

4:7-Dimethylcoumarin-6-azonaphthylsulphoarsinic acid, prepared in a similar manner from 4 : 7-dimethyl-6-aminocoumarin and naphthylsulphoarsinic acid, recrystallised from acetic acid in yellow microcrystalline powder, m.p. 204° (decomp.). (Found : N, 5.18 ; As, 13.85. $C_{21}H_{17}O_8N_2$ SAs requires N, 5.2 ; As 14.09 per cent.).

1 : 2- α -Naphthapyrone-6-azonaphthylsulphoarsinic acid was prepared in a similar way from 6-amino-1 : 2 α -naphthapyrone and naphthylsulphoarsinic acid. The only modification that was necessary was that the diazotised solution was filtered cold before coupling. The compound was crystallised from acetic acid to a mass of yellow microcrystalline powder shrinking at 170° . (Found : N, 4.7 ; As, 12.98. $C_{23}H_{15}O_8N_2$ SAs requires N, 5.05 ; As, 13.53 per cent.).

4-Methyl-1 : 2- α -naphthapyrone-6-azonaphthylsulphoarsinic acid.—The method of preparation of this compound is the same as the previous compounds. But as the hydrochloride of the base is sparingly soluble in water the diazotisation was effected in presence of excess of ice in suspended solution. The compound was crystallised from acetic acid in yellow powder, m.p. 162° (decomp.). (Found : N, 4.6 ; As, 13.1. $C_{24}H_{17}O_8N_2$ SAs requires N, 4.9 ; As, 13.2 per cent.).

My sincerest thanks are due to Dr. M. Goswami, for his keen interest and valuable suggestions and to the Director of Public Instruction, Bengal, for awarding me a Post Graduate Research Scholarship which has enabled me to undertake the work.

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Synthesis of Aloe-emodin.

By P. C. MITTER AND DILIPKUMAR BANERJEE.

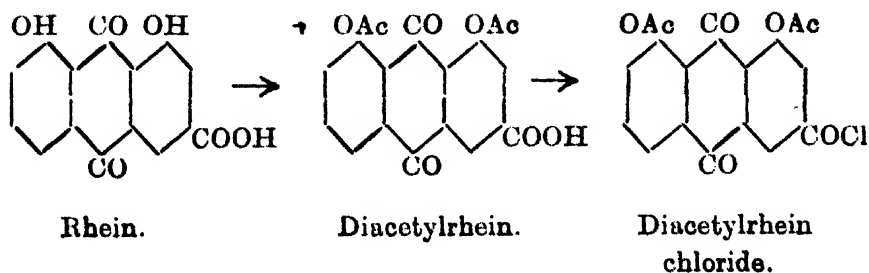
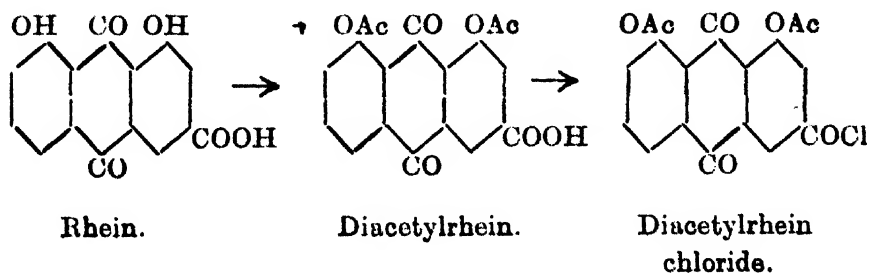
Among the hydroxyanthraquinones occurring in nature, aloemodin, the active principle of aloes, rhubarb, etc., occupies a peculiar position, because of the presence of a carbinol group. The constitution of this substance has been determined by Oesterle and others (*Arch. Pharm.*, 1911, **249**, 445) by converting it into chrysophanic acid by reduction and into rhein by oxidation.

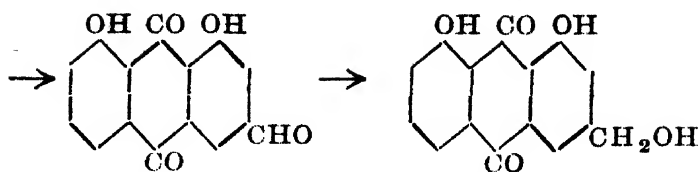
The authors have confirmed this constitution by actual synthesis, taking as the starting point rhcin which has been already synthesised (Eder and Widmer, *Helv. Chim. Acta*, 1922, 5, 3) and reducing it through the chloride and the aldehyde into the corresponding alcohol.

In order to determine the conditions of the experiment, the authors reduced anthraquinone- β -carboxylic acid through the chloride into anthraquinone- β -aldehyde by the method of Rosenmund and his co-workers (*Ber.*, 1918, **51**, 585; 1921, **54**, 425), using sulphurised quinoline as an anti-catalyst. The yield of aldehyde was, however, poor and it was subsequently found that the reaction goes on much better without any anti-catalyst.

Anthraquinone- β -aldehyde could be successfully reduced to anthraquinone- β -carbinol with hydrogen in presence of platinum oxide with ferrous chloride as promoter, according to the method of Roger Adams and his co-workers (*J. Amer. Chem. Soc.*, 1922, **44**, 1397 ; 1923, **45**, 1071, 2171 ; 1924, **46**, 1675).

The synthesis of aloe-emodin was accomplished, according to the following scheme.





1:8-Dihydroxyanthraquinone-
3-aldehyde.

Aloe-emodin.

EXPERIMENTAL.

Anthraquinone- β -carboxylic acid chloride.—Anthraquinone- β -carboxylic acid (5 g.), prepared by oxidising β -methylantraquinone with chromic acid in acetic acid solution, was heated with thionyl chloride (100 g.) on a water-bath until the evolution of hydrochloric acid ceased. The excess of thionyl chloride was distilled off under diminished pressure and the acid chloride crystallised from benzene, m.p. 146° , yield theoretical.

Anthraquinone- β -aldehyde.—The acid chloride (2 g.), palladiumised barium sulphate (0.7 g.) containing 5 p.c. palladium and dried in *vacuo* over phosphorus pentoxide were taken in about 40 c.c. of dry xylene in a round bottomed flask with a side-tube having a glass tube ground into it and reaching to the bottom of the flask. The flask, which was provided with a reflux condenser, was heated in an oil-bath at $150-60^{\circ}$. Hydrogen, carefully purified and dried by passing through strong sulphuric acid and finally through two Peligot tubes containing phosphorus pentoxide, was passed into the mixture through the side-tube until the ensuing gas was free from hydrochloric acid. The solution was then filtered from the catalyst and shaken on the machine with 10 p.c. sodium bisulphite solution. The bisulphite layer was then separated and decomposed with hydrochloric acid, m.p. 186° , yield 1g.

For studying the conversion of the aldehyde into the carbinol, anthraquinone- β -aldehyde was prepared on a large scale directly from β -methylantraquinone (Ullmann and Klingenberg, *Ber.*, 1913, 46, 712).

Anthraquinone- β -carbinol.—Anthraquinone- β -aldehyde (2 g.) was dissolved in absolute alcohol, platinum oxide (0.1725 g.) prepared according to the method of Roger Adams (*loc. cit.*) was added and then 0.1 millimole of ferrous chloride. The flask containing the mixture was evacuated by means of a water-pump until the solution began to boil and then connected with a gas holder containing pure hydrogen and shaken mechanically until the theoretical amount of hydrogen

was absorbed, which in this case took only *five minutes*. The catalyst was then removed by filtration, the alcohol evaporated off and the residue treated with boiling water in which the carbinol was found to be soluble. On recrystallising from benzene it was obtained as a yellow crystalline powder, m.p. 183° . (Found: C, 75.52; H, 3.9. $C_{15}H_{10}O_3$ requires C, 75.63; H, 4.2 per cent.).

Diacetylchrysophanic acid.—Chrysophanic acid was prepared from crude chrysarobin according to the method of Fischer and Gross (*J. pr. Chem.*, 1911, ii, 84, 369). It was acetylated by dissolving in acetic anhydride, cooling and adding 2 or 3 drops of strong sulphuric acid. The acetylation was almost instantaneous.

Diacetylrhein.—It was prepared by oxidising diacetylchrysophanic acid according to the method of Fischer and Gross (*loc. cit.*). On treating the product with dilute soda solution and acidifying, a mixture of rhein and diacetylrhein was obtained which was completely deacetylated by boiling with alcoholic potash, the rhein recrystallised from pyridine and reacetylated by heating with acetic anhydride and pyridine.

Diacetylrhein chloride.—It was prepared by treating diacetylrhein with thionyl chloride in the usual manner. Crystalline mass from benzene, m.p. 190° . (Found: Cl, 8.7. $C_{19}H_{11}O_7Cl$ requires Cl, 9.2 per cent.).

1:8-Dihydroxyanthraquinone-3-aldehyde.—Diacetylrhein chloride was reduced to the aldehyde according to Rosenmund's method (*loc. cit.*). On decomposing the bisulphite compound by boiling with hydrochloric acid, the substance was simultaneously deacetylated. From 2 g. of the acid chloride 0.7 g. of the aldehyde was obtained. Brown glistening needles from glacial acetic acid, m.p. 218° . (Found: C, 66.85; H, 3.0. $C_{15}H_8O_5$ requires C, 67.16; H, 3.0 per cent.).

1:6-Dihydroxyanthraquinone-3-carbinol (Aloe-emodin).—The reduction of the aldehyde was effected exactly in the same way as with anthraquinone- β -aldehyde. The carbinol was recrystallised first from dilute acetic acid and then from toluene. Orange needles from toluene, m.p. $219-20^{\circ}$ (corr.).^{*} The m.p. was not depressed by admixture with natural aloe-emodin from Barbadoes aloes, melting at 221° (corr.). (Found: C, 67.08; H, 3.5. $C_{15}H_{13}O_5$ requires C, 66.66; H, 3.7 per cent.).

Kinetics of the Reaction Between Bromacetate and Thiosulphate Ions at Great Dilutions.

BY A. N. KAPPANNA AND H. W. PATWARDHAN.

In a previous communication by one of us (*J. Indian Chem. Soc.*, 1929, **6**, 45) the results of a study of the kinetics of the reaction between bromacetate and thiosulphate ions in very dilute solutions were presented. It was found there that the variation of the kinetic activity factor with ionic strength in the region 0.0025μ — 0.012μ was quantitatively in accordance with the predictions of the Brönsted-Debye theory. Nine months after the publication of the above paper, La Mer published his work on the same reaction (*J. Amer. Chem. Soc.*, 1929, **51**, 3341, and correction, 1929, **51**, 3678) and his results indicate that $\frac{d \log k}{d \sqrt{\mu}}$ observed is only threefourths of what is predicted by the Brönsted-Debye theory. The discrepancy between these two sets of results is very great in view of the fact that very accurate results could be obtained in the kinetic measurements of the reaction. The importance of the subject and the far-reaching effects of the general application of the Brönsted-Debye theory are such that we thought it necessary to revise and extend the previous work on this reaction. In this communication we are presenting data obtained over a wide range of temperatures (30° — 90° .)

EXPERIMENTAL.

The experimental procedure adopted was the same as in our previous investigation (*loc. cit.*).

The sodium bromacetate was prepared as follows:—Kahlbaum's bromacetic acid dried over phosphorus pentoxide was dissolved in pure dry ether so as to make a concentrated solution. To this was added a drop of phenolphthalein solution and then an almost saturated solution of sodium ethoxide in absolute alcohol drop by drop, the mixture being well stirred, until the liquid turned faint pink. Most of the sodium salt formed appeared as precipitate. Next, the mixture was treated with a drop or two of the acid solution to just decolourise the indicator and the precipitate filtered rapidly under a suction and washed with dry ether. The salt thus obtained

was next dissolved in the minimum quantity of absolute alcohol and reprecipitated by the addition of ether. A considerable amount of the salt was thus obtained. It was next filtered, washed with dry ether and the adherent ether was removed by evaporation in vacuum. The salt was preserved in a dish over fused calcium chloride in a desiccator. The purity of the salt was tested by the estimation of bromine in a definite amount of the salt.

Solutions of different concentrations were prepared by weighing out exact quantities of the salt. All the solutions were prepared in conductivity water.

The reaction was followed by adding to known volumes of the reaction mixture, definite amounts of a standard centinormal solution of iodine and titrating the excess of iodine against centinormal thiosulphate.

While working at temperatures above 50° , solutions of sodium bromacetate of different concentrations were kept alongside the reaction mixtures for the same periods of time as the latter to find out if any side reaction (the replacement of bromine in the bromacetate ion by hydroxyl by interaction with water) took place. It was found in all cases that no such action had taken place in the solutions at the concentrations covered by the investigations in this paper.

Table I contains a summary of the results at different temperatures. The figures included in brackets under 30° , 40° and 50° are velocity constants obtained in our previous investigation. It will be observed that the agreement between the two sets of results is quite close.

TABLE I.

0.484 K.

μ	30°	40°	50°
0.00125	—	—	—
0.00250	0.1940 (0.1960)	0.4420 (0.4400)	0.9750 (0.0996)
0.0050	0.2153 (0.2140)	0.4980 (0.4980)	1.080 (1.150)
0.0070	0.2307 (0.2300)	0.5224 (0.5290)	1.156 (1.213)
0.0085	0.2410 (0.244)	0.5460 (0.5400)	1.210 (1.280)
0.0100	0.2510 (0.256)	0.5690 (0.577)	1.260 (1.320)
0.0140	0.2680 (0.275)	0.6330 (0.6310)	1.436 (1.480)
0.0200	0.3040 (0.310)	0.6900 (0.6780)	1.577 (1.600)

TABLE I—(contd.)

0°434 K.

μ	60°	70°	80°	90°
0·00125	1·880	3·759	7·050	12·90
0·00250	2·050	4·000	7·595	14·10
0·0050	2·290	4·544	8·560	15·67
0·0070	2·440	4·876	9·030	16·99
0·0085	2·540	5·140	9·440	17·86
0·0100	2·650	5·290	9·910	18·50
0·0140	3·078	6·095	11·400	21·14
0·0200	3·328	6·590	12·320	22·85

Discussion of Results.

Log K plotted against $\sqrt{\mu}$ gives straight lines in all cases over the region $\sqrt{\mu}=0\cdot03537$ to $\sqrt{\mu}=0\cdot11$ (for the region $0\cdot00125\mu-0\cdot012\mu$) for data at all temperatures. The slopes of the curves $\left(\frac{d \log k}{d \sqrt{\mu}} \right)$ obtained from these curves are compared in Table II with the slopes calculated from the standpoint of Debye-Hückel theory at different temperatures.

TABLE II.

Temperature	30°	40°	50°	60°	70°	80°	90°
Slope (found)	2·16	2·20	2·23	2·28	2·29	2·29	2·30
Slope (calc.)	2·07	2·12	2·18	2·23	2·29	2·31	2·36

The agreement between the two sets of values is as good as can be expected from the nature of the work.

It can, therefore, be definitely stated that in aqueous solutions for the ions involved in this reaction, the variation of the kinetic activity factor with ionic strength in the region $0\cdot00125\mu-0\cdot012\mu$ is in good agreement with the predictions of the Brønsted-Debye theory over a wide range of temperatures up to 90°.

Temperature coefficient of the reaction rate.—The temperature coefficient of the reaction rate, throughout the temperature range examined, has been found to be practically independent of ionic strength. Table III gives the average temperature coefficient at different temperature limits.

TABLE III.

$\frac{K_{40}^{\circ}}{K_{30}^{\circ}}$	$\frac{K_{50}^{\circ}}{K_{40}^{\circ}}$	$\frac{K_{60}^{\circ}}{K_{50}^{\circ}}$	$\frac{K_{70}^{\circ}}{K_{60}^{\circ}}$	$\frac{K_{80}^{\circ}}{K_{70}^{\circ}}$	$\frac{K_{90}^{\circ}}{K_{80}^{\circ}}$
2.280	2.205	2.102	1.999	1.87	1.85

These values for temperature coefficients lead to an average value of 15680 calories for the energy of activation of the two reacting ions.

Summary.

A detailed study of the kinetics of the reaction between brom-acetate and thiosulphate ions in the presence of sodium ions has been made over the temperature range 30°-90° in the region of ionic strengths 0.00125 μ -0.02 μ in aqueous solutions.

At all temperatures, the variation of the kinetic activity factor with ionic strength in the region 0.00125 μ -0.012 μ for the ions involved in this reaction has been found to be in good agreement with the predictions of the Brönsted-Debye theory.

The energy of activation of the two reacting ions has been found to be 15680 calories, from the temperature coefficient of the reaction rates at different temperatures.

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Chemical Examination of the Seeds of *Abrus precatorius*, Linn. Part I.

BY NARENDRANATH GHATAK AND RAMJEE KAUL.

Abrus precatorius or Jequirity as it is known in English, Gunja in Sanskrit, Rati in Hindustani and Kunch in Bengali is a plant of the natural order *Leguminosæ*. It is grown in India and other hot countries. It is a perennial twiner with numerous stems. Seeds from 3 to 5 are contained in pods which are from $1\frac{1}{4}$ to $1\frac{1}{2}$ in. long and $\frac{1}{2}$ in. wide. The seeds are usually bright scarlet, with a black spot on the top and are highly polished. The average weight of the seed is 1.75 grains. There are three varieties of the seed e.g., scarlet, white and black, but the findings of the present paper are on the scarlet one. The seeds are used in India by the goldsmiths as weight. The leaves, seeds and the roots of *Abrus precatorius* have been articles of Hindu materia medica from a very remote period. Internally, the seeds are described as poisonous and useful in affections of the nervous system, and, externally, in skin diseases, ulcers, affections of the hair, leprosy, etc., (Dymock, "Pharmacographia Indica," Vol. I. p. 430).

Warden and Waddell ("Non-bacillar nature of Abrus poison," Calcutta, 1884) have given the name 'abrin' to the poisonous principle of Jequirity. They showed that abrin was closely allied to 'plant albumin' but did not enter into any details as to whether it consisted of one or more proteids. Martin (*J. Chem. Soc.*, 1887, 52, 990) proved the presence of two proteids, a globulin and an albumose in the kernels and the toxic action of Jequirity is attributed to them. Dr. Warden ("Pharmacographia Indica," 1890, Vol. I, p. 442) claims to have succeeded in isolating an acid from the seeds, which he named as 'abric acid' and represented it by the formula $C_{21}H_{24}O_4N_3$, which is not in agreement with the "law of even number of atoms." He also obtained a small quantity of pungent volatile oil. But he gives no details as to how abric acid was isolated. Abrin (Haas and Hill, "Chemistry of Plant Products," 1928, Vol. I. p. 371) has been suspected to have the same properties as ricin which occurs in *Ricinus*.

Their toxic characters have been attributed partly to the presence of ptomaine bodies and largely to bacterial toxins, a class of substance related to albumoses.

The above represents the work that has hitherto been done on the seeds of *Abrus precatorius*. A systematic analysis of the seeds was, therefore, undertaken with a view to study the exact chemical nature of the poisonous constituents. Two definite products, one nitrogen containing and another a glucoside, *viz.*, abrine and abralin, have now been isolated. Some quantity of a non-drying yellow oil has also been obtained. The properties of these substances have been described in the experimental part.

EXPERIMENTAL.

The scarlet variety of the seed of *Abrus precatorius* was obtained from the local market. The red seed-coat was removed by coarsely crushing the seeds in a grinding machine. The outer coating constituted 30 p. c. of the entire seed. The yellow kernels were very hard.

The powdered kernel (50 g.) was freed from oil by extraction with petroleum ether in the cold and the oil-free powder on cold aqueous extraction gave a cloudy precipitate with ethyl alcohol which probably contained some enzymes. The powder on completely burning left 2.5 p. c. of a white residue (ash) which on qualitative analysis was found to contain iron, aluminium, calcium, silicon, magnesium, sulphate and phosphate.

For complete analysis 1.5 kg. of the crushed kernels were exhaustively extracted in a round bottomed extraction flask with 5 litres petroleum ether (b. p. 35-60°) till a portion of the extract did not give any oily residue on evaporation of the solvent. From the petroleum ether extract 85 g. of a yellowish brown, pungent, non-drying oil was obtained. The oil-free powder was successively extracted with rectified spirit. The first few extracts were yellow in colour and after that colourless extracts were obtained which deposited white needles in small quantities on evaporation of the solvent. The substance seemed to be very little soluble in alcohol and, therefore, the extraction was done about 20 times in order to recover the crystalline product completely from the powder. The powder became almost colourless after the extractions. The total alcoholic extract was concentrated under reduced pressure when a brown syrup having white crystalline suspension was obtained. The liquid, which had a

disagreeable smell, was allowed to stand for about a week when the quantity of the crystalline product increased and settled at the bottom. It was filtered and washed with water. The dried crude product, which weighed 13 g. turned brown at 210° and completely melted at 247° . This substance was moderately soluble in hot water from which snow-white needles were obtained melting at 295° and having a molecular formula $C_{12}H_{14}O_2N_2$. It has been named as 'abrine' by the present authors. Warden (*loc. cit.*) must have got this substance in an impure form which gave him a wrong analytical data and made him to suspect the compound to be acidic in nature.

• Abrine is insoluble in all organic solvents excepting alcohol in which it is slightly soluble. Neutral ferric chloride, lead acetate or subacetate, silver nitrate and calcium chloride have no effect on the substance. Phosphomolybdic acid produces a white precipitate which soon changes to yellowish green and finally to grey colour. Eardman's and Fröhde's reagents give yellow coloration with abrine. Gold chloride solution produces a yellowish turbidity which darkens and in about 1 minute becomes violet, which, however, throws down a blue-black precipitate on addition of concentrated hydrochloric acid. Platinic chloride solution seems to have no effect on the substance in the cold, but on heating and allowing it to cool a brown gelatinous precipitate settles at the bottom. Abrine is non-respondent to the rest of the alkaloidal reagents. It dissolves readily in hydrochloric acid and on complete evaporation of the solvent long silky needles of the hydrochloride of abrine are obtained which quickly dissolve in water. The hydrochloride gives all the reactions of the free base as described above, excepting with gold and platinic chloride solutions. The hydrochloride, however, gives a white precipitate with phosphotungstic acid which turns brown in about 5 minutes. From the above reactions it can be said that abrine, is semi-alkaloidal in character. It is tasteless when pure and therefore may be classed in the group of non-bitter alkaloids.

The thick mother liquor after the separation of abrine was diluted with water and on addition of lead acetate solution a thick yellow flocculent precipitate of strong disagreeable odour, was obtained. The precipitate was washed free from lead and decomposed with sulphuretted hydrogen. The yellow filtrate on complete evaporation of water gave a brown sticky mass from which no chemically pure substance could be isolated. The product contained considerable amount of reducing sugars.

The filtrate of the above lead salt gave a bright yellow bulky precipitate with lead subacetate solution. The purified lead salt was decomposed with sulphuretted hydrogen in alcoholic suspension. The yellow filtrate was concentrated under reduced pressure and on complete evaporation of the solvent a yellow deposit was obtained. It was non-crystalline in character and melted at 105° after remaining over calcium chloride in a vacuum desiccator for 2 days. This substance which has a molecular formula $C_{13}H_{14}O_7$, has been named as 'abralin' by the present authors. Abralin does not reduce Fehling's solution and Tollen's reagent, but both are readily reduced if the compound is previously hydrolysed by warming with concentrated hydrochloric acid. It does not produce any coloration or precipitate with the usual alkaloid reagents. Abralin has an astringent and mild bitter taste and produces a dark coloration with neutral ferric chloride solution, which turns red on dilution. The physiological examinations of abrine and abralin are in progress.

The oil on purification with Fuller's earth and animal charcoal became lighter in colour. It did not contain nitrogen and sulphur and was tasteless. The oil was optically active and gave a *dextro* rotation of $[\alpha]_D^{25} = +0.39$. This small rotation must be due to the presence of sterols in the oil. The oil burnt with an absolutely non-luminous flame and gave the following constants.

Mixture	0.78 p. c.
Specific gravity at 25°	0.9139
Refractive index at 25°	1.4662
Acid value	2.44
Saponification value	191.7
Hehner value	88.06
Acetyl value	nil
Iodine value	95.1
Unsaponifiable matter	1.68

Abrine.—Abrine dissolves in concentrated nitric acid with orange red colour which becomes yellow on dilution. In strong sulphuric acid it dissolves with yellow colour. When very slowly crystallised from water about 1 cm. long star shaped needles are obtained. [Found: C, 65.78; H, 6.46; N, 13.15; M. W. (cryoscopic in phenol),

221. $C_{12}H_{14}O_9N_2$ requires, C, 66.08; H, 6.42; N, 12.84 per cent. M.W., 218).

Abralin.—In concentrated nitric acid abralin dissolves with red colour, which becomes orange yellow on dilution. In strong sulphuric acid it dissolves with a yellow colour which slowly darkens and finally becomes deep red. On dilution the colour is discharged and a yellow flocculent precipitate separates, which is the aglacone of the glucoside. Abralin was optically active, having a *laevo* rotation of $[\alpha]_D^{25} = -27.37$ in aqueous solution. [Found: C, 54.98; H, 5.29; M. W. (cryoscopic in phenol), 286, (lead salt), 281. $C_{13}H_{14}O_7$ requires, C, 55.32; H, 4.96 per cent. M.W., 282). •

• Further work on the constitutions of abrine and abralin is in progress.

Our best thanks are due to Dr. S. Dutt, D.Sc., P.R.S., for the kind interest he has taken in the work. One of us (N.G.) wishes to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship which enabled him to take part in the investigation.

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Synthesis of Chromones. Part III. Condensation of β -Naphthol with Alkyl Acetoacetic Esters.

BY DURJAHARAN CHAKRAVARTI.

The condensation of phenols with β -ketonic esters in presence of sulphuric acid (Pechmann reaction) and in presence of phosphorus pentoxide (Simonis reaction) has been the subject of investigation by the author (*J. Indian Chem. Soc.*, 1931, 8, 129, 407, 619; 1932, 9, 25, 31) and discussion, excepting a generalisation (*ibid.*, 1932, 9, 32) regarding these reactions was postponed until the accumulation of further experimental data. In the meantime, Robertson and his collaborators (*J. Chem. Soc.*, 1931, 1256, 1877, 2426; 1932, 1180, 1681) arrived at the conclusion that the Simonis reaction depends entirely on the nature of the phenol and is independent of the nature of the ester; which view was afterwards discarded by the same authors (*J. Chem. Soc.*, 1932, 1180). While studying the β -naphthopyrones, Dey and Lakshminarayanan (*J. Indian Chem. Soc.*, 1932, 9, 153) have supported the earlier view of Robertson and others that "The important factor, which determines the course of the condensation, however, is obviously not the β -ketonic ester but the phenol itself, as suggested by Robertson."

That the course of these reactions, however, depends on *both* the phenol and the β -ketonic ester, is shown by the following experimental facts.

Esters.	Products with H_2SO_4 . with β -naphthol.	Products with P_2O_5 .
Ethyl acetoacetate	Mixture of coumarin and chromone (Dey and Lakshminarayanan, <i>loc. cit.</i>).	Chromone (Dey and Lakshminarayanan, <i>loc. cit.</i>).
Ethyl α -methylacetoacetate	Coumarin in poor yield*	Chromone *
Ethyl α -ethyl (or α -propyl or α -isopropyl)-acetoacetate	No reaction*	Chromones *

* *vide infra*.

Esters.	Products with H_2SO_4 . with m-cresol.	Products with P_2O_5 .
Ethyl acetoacetate	Coumarin (Fries and Klostermann <i>Ber.</i> , 1906, 39, 971).	Coumarin (Chakravarti <i>J. Indian Chem. Soc.</i> , 1932, 9, 26; Robertson and others, <i>J. Chem. Soc.</i> , 1932, 1681).
Ethyl α -methylacetoacetate	Coumarin in poor yield (Fries and Klostermann, <i>Annalen</i> , 1908, 362, 3).	Chromone (Petschek and Simonis, <i>Ber.</i> , 1913, 46, 2014).
Ethyl α -propyl (or α -isopropyl or α -isobutyl)-acetoacetate	No reaction (Chakravarti, <i>J. Indian Chem. Soc.</i> , 1932, 9, 32).	No product can be isolated from the reaction mixture.
with p-cresol.		
Ethyl acetoacetate	Coumarin (Pechmann and Cohen, <i>Ber.</i> 1884, 17, 2187).	Coumarin (Robertson and Sandrock, <i>J. Chem. Soc.</i> , 1932, 1480).
Ethyl α -methylacetoacetate	Coumarin (Chakravarti, <i>J. Indian Chem. Soc.</i> , 1932, 9, 29).	Chromone (Petschek and Simonis, <i>loc. cit.</i>).
Ethyl α -ethylacetoacetate	Coumarin in poor yield (Robertson and Sandrock, <i>loc. cit.</i>).	Chromone (Robertson and Sandrock, <i>loc. cit.</i>).
Ethyl α -propyl (or isopropyl) acetoacetate	No reaction (Chakravarti, <i>J. Indian Chem. Soc.</i> , 1932, 9, 31).	No product can be isolated from the reaction mixture.
Ethyl α -chloroacetoacetate	Coumarin	Coumarin (Robertson and Sandrock, <i>loc. cit.</i>).

The present paper describes the β -naphthapyrones prepared by the condensation of β -naphthol with alkyl acetoacetic esters. The β -naphthachromones are characterised by the formation of 2-styryl derivatives, which distinguish them from the isomeric coumarins (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1931, 8, 131). The generalisation, previously recorded, holds in this case also. β -Naphthol does not react readily with acetoacetic ester in presence of sulphuric acid to form coumarins, and it forms chromones in comparatively good yield in presence of phosphorus pentoxide.

The condensation of phenols with other β -ketonic esters, *e.g.*, acetone dicarboxylic ester, oxalacetic ester, benzoylacetic ester and acetosuccinic ester, in presence of phosphorus pentoxide is being studied and the results will be communicated shortly.

EXPERIMENTAL.*

3:4-Dimethyl-1:2- β -naphthapyrone.—A mixture of β -naphthol (5 g.) and ethyl α -methylacetoacetate (5 g.) was slowly added to ice-cold concentrated sulphuric acid (12 c.c.) and the solution was shaken. The solution was kept for 48 hours and crushed ice added to it; only a small amount of solid separated on standing. This was crystallised from dilute alcohol as colourless needles, m.p. 127°. (Found: C, 80.12; H, 5.53. $C_{15}H_{12}O_2$ requires C, 80.35; H, 5.35 per cent.).

2:3-Dimethyl-1:4- β -naphthapyrone.—To a warm solution of β -naphthol (10 g.) and ethyl α -methylacetoacetate (10 g.), phosphorus pentoxide (25 g.) was gradually added and the mass shaken. The mass became hot and on standing for 15 minutes, it was heated on the water-bath for about 1 hour. Crushed ice was then added and the thick oil treated with cold caustic soda solution, when solid separated. It was thoroughly washed with water, dried and crystallised from rectified spirit in colourless plates, m. p. 130° (mixed with the coumarin, m. p. 95°). (Found: C, 80.22; H, 5.41. $C_{15}H_{12}O_2$ requires C, 80.35; H, 5.35 per cent.).

2-Styryl-3-methyl-1:4- β -naphthapyrone.—A solution of 2:3-dimethyl-1:4- β -naphthapyrone (1 g.) in absolute alcohol was treated with alcoholic sodium ethoxide (0.5 g. sodium) and benzaldehyde (1 g.), when only a slight yellow colouration was produced. The solution, on keeping overnight, deposited yellow crystals, which were filtered off, washed with dilute alcohol and recrystallised from absolute alcohol in long yellowish silky needles, m. p. 186°. (Found: C, 84.32; H, 4.91. $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.12 per cent.).

The 3:4-dimethyl-1:2- β -naphthapyrone, prepared with sulphuric acid, does not react with benzaldehyde.

2-Methyl-3-ethyl-1:4- β -naphthapyrone was prepared from β -naphthol and ethyl α -ethylacetoacetate in presence of phosphorus pentoxide and isolated in the manner described above. It crystallised from dilute alcohol in colourless plates, m. p. 117°. (Found: C, 80.22; H, 5.95. $C_{16}H_{14}O_2$ requires C, 80.67; H, 5.88 per cent.).

2-Styryl-3-ethyl-1:4- β -naphthapyrone was prepared by condensing the above pyrone with benzaldehyde as usual. It crystallised in yellowish silky needles from absolute alcohol, m. p. 183°.

* The β -naphthapyrones have been named according to Day and Lakshminarayana (loc. cit.).

(Found: C, 84.35; H, 5.32. $C_{23}H_{18}O_2$ requires C, 84.66; H, 5.51 per cent.).

2-Methyl-3-propyl-1:4- β -naphthapyrone, the condensation product of β -naphthol and ethyl α -propylacetoacetate in presence of phosphorus pentoxide, crystallised from rectified spirit as colourless needles, m. p. 95°. (Found: C, 81.12; H, 6.1. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35 per cent.).

2-Styryl-3-propyl-1:4- β -naphthapyrone crystallised from rectified spirit in yellow silky needles, m. p. 168°. (Found: C, 84.35; H, 5.98. $C_{24}H_{20}O_2$ requires C, 84.70; H, 5.88 per cent.).

2-Methyl-3-isopropyl-1:4- β -naphthapyrone was prepared by condensing β -naphthol and ethyl α -isopropylacetoacetate in presence of phosphorus pentoxide. It crystallised from rectified spirit in colourless prismatic needles m. p. 131°. (Found: C, 80.83; H, 6.43. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35 per cent.).

2-Styryl-3-isopropyl-1:4- β -naphthapyrone crystallised from rectified spirit as silky yellow needles, m. p. 187°. (Found: C, 84.53; H, 5.67. $C_{24}H_{20}O_2$ requires C, 84.70; H, 5.88 per cent.).

β -Naphthol does not condense with ethyl α -ethyl (or α -propyl or α -isopropyl)-acetoacetate in presence of sulphuric acid.

My best thanks are due to Prof. R. N. Sen for his interest in this investigation and to Drs. P. Neogi and M. Q. Khuda for giving me full facilities for conducting this work.

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Studies in Organo-arsenic Compounds. Part II.

By HIRENDRA NATH DAS-GUPTA.

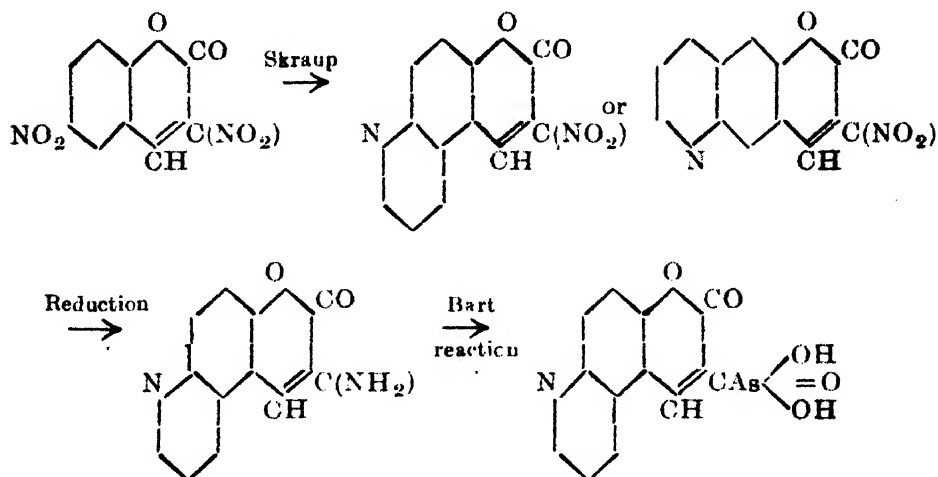
No attempt appears hitherto have been made to introduce arsenic into xanthone nucleus. The only compound that is known to contain arsenic is xanthoarsenite, a naturally occurring mineral, discovered by Igelström (*Z. Kryst. Min.*, 1886, 10, 518).

Xanthone itself possesses antiseptic action and the assumption that by introducing arsenic into the nucleus, the resulting compounds might prove to have greater potentialities as drugs, led to the present attempts. The different compounds that have been prepared are the following: Xanthone-3-arsinic acid, α -nitroxantharsinic acid, β -nitroxantharsinic acid, β -aminoxantharsinic acid, β -acetylaminoxantharsinic acid, and bromonitroxantharsinic acid.

The next series of compounds that have been described are the quinoline derivatives of coumarin and xanthone containing arsenic in the nucleus. Of these the first compound is a pseudo oxazone and contains, in addition to the pyridine ring, groups like-CH:CH-and -O·CO in the ring. The existence of the above mentioned groupings in a compound causes the augmentation of the number of polymorphonuclear white blood corpuscles, helping there by in an indirect way, in checking an attack due to parasites, and increased internal secretions. It has also been definitely established that quinoline compounds have decided antpyretic action, specially if the position-6 is fixed and an enhanced action is observed if both 4- and 6-positions are simultaneously occupied. The compound ψ -1:8-isonaphthoxazone-3-arsinic acid, described in this paper, in which the positions 4 and 6 are occupied, satisfy all the above mentioned conditions in addition to the pentavalent arsenic in the nucleus and was, therefore, supposed to have an enhanced antipyretic and bactericidal action in the treatment of diseases due to parasitic organism.

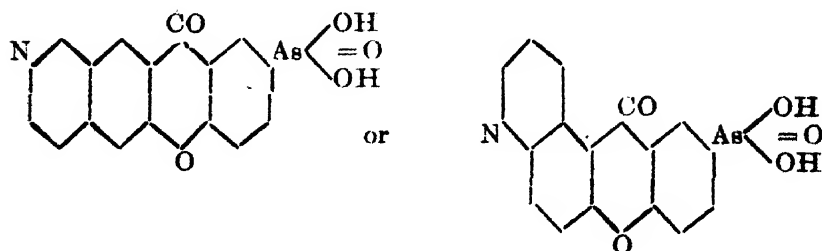
The nitro- ψ -1:8-isonaphthoxazone was prepared according to the method of Dey and Goswami (*J. Chem. Soc.*, 1919, 115, 531) for the preparations of coumaroquinoline from nitrocoumarins. The provisional formula as advanced by the authors (*loc. cit.*) has been adopted.

The reduction of the nitro- ψ -oxazone was effected by sulphuretted hydrogen and ammonia in alcoholic solution. It is probable that upto the formation of the arsenic acid derivative the following has been the main course.



The application of the Skraup reaction was extended to the other dinitro derivatives of coumarin, *e.g.*, 7-methyl- and 4:7-dimethyl-3:6-dinitrocoumarins and in each case the desired product was obtained but the yield was too low to be used for subsequent treatments.

The second compound xanthoquinoline- β -arsinic acid was prepared from β -aminoxanthoquinoline. The nitro compound was prepared by Dhar (*J. Chem. Soc.*, 1920, 117, 1053). Here also it will be found that the position -4 or 6 is occupied and from similar arguments should have antiseptic and bactericidal activity as will be evident from the following constitutional formula.



The arsenic acids, enumerated as above, had all been prepared by the well-known Bart's reaction from their corresponding amino derivatives. The reduction of β nitroxantharsinic acid was done by the

method of Jacob, Heidelberger and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1580) most easily. The method claimed by Fargher (*J. Chem. Soc.*, 1919, **115**, 990) to give satisfactory results and which is a modification of that described in D. R. P. 224958, for the method of reduction of nitroarsinic acids failed to do the same in this particular case. Monobromodinitroxanthone and β -nitroxanthoquinoline had been reduced by ammonia and sulphuretted hydrogen in alcoholic solution. The method for the reduction of 3-nitroxanthone, α - and β -dinitroxanthone, as suggested by Dhar (*J. Chem. Soc.*, 1916, **109**, 744), gave very low yield of the amino derivatives. The additional disadvantage of the method is that on account of the lower solubility of the nitrocompounds in alcohol, a large quantity of the solvent is required to start with. To obviate this difficulty the nitro derivatives had been reduced by stannous chloride in alcohol and hydrochloric acid solution. In the cases of α - and β -derivatives, contrary to the usual expectation, namely, the simultaneous reduction of both the nitro groupings, in each case a nitroamino compound was obtained. The reduction products were tested both qualitatively and quantitatively to ascertain the similarity of the compounds with those obtained by reducing with sulphuretted hydrogen and ammonia as tried by Dhar (*loc. cit.*) and the identity was observed in each case.

The arsenic acids vary in coloration, from brown to yellow, and most of them are nearly insoluble in commoner organic solvents. They are all microcrystalline solids, readily soluble in caustic alkalis and alkaline carbonates. The alkaline solutions are deep brown in colour from which hydrochloric acid precipitates the original compounds.

EXPERIMENTAL.

Reduction of Nitroxanthones.

3-Aminoxanthone.—3-Nitroxanthone (7 g.) was gradually added to a mixture, consisting of stannous chloride (21 g.), alcohol (20 c.c.) and concentrated hydrochloric acid (18 c.c.), heated in a beaker to a clear solution by direct flame. While the addition of the nitro compound was made the flame was turned low. Within a very short time a slow reaction began and this was over when every thing went into solution. To the reaction mixture concentrated hydrochloric acid (36 c.c.) was added whereby light yellowish white feathery mass immediately separated out. This was allowed to cool and then

filtered. The residue was washed repeatedly with concentrated hydrochloric acid and was then dissolved by boiling in excess of water and filtered. The filtrate was cooled somewhat and sulphuretted hydrogen was passed to precipitate the tin. The resulting mixture was filtered and treated with ammonia when a yellow precipitate of 3-aminoxanthone was obtained. The amino compound was separated, dried, and crystallised from alcohol, m. p. 232°. The other properties of the compound were found to tally with that prepared by Dhar (*loc. cit.*).

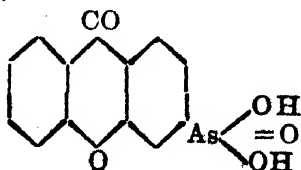
α-Nitroaminoxanthone was prepared in a similar manner as above, with the following reaction mixture: *α*-dinitroxanthone (7.5 g.), stannous chloride (22 g.), hydrochloric acid (20 c.c.) and alcohol (30 c.c.). Towards the end of the reaction 35 c.c. more of the concentrated hydrochloric acid were added. The reaction was a rapid one and only one of the nitro groups underwent reduction to amino compound. The substance was crystallised from alcohol, m. p. 205°. 07°. (Found: N, 10.78. $C_{13}H_8O_4N_2$ requires N, 10.9 per cent.).

β-Nitroaminoxanthone was prepared in a similar manner and with the same proportions as the *α*-derivative, m.p. 264-65°.

Monobromonitroaminoxanthone.—The reduction of the monobromodinitroxanthone was effected by sulphuretted hydrogen and ammonia in alcoholic solution. The substance was sparingly soluble in alcohol and hence a large excess of the solvent was required. The addition of ammonia was made in two or three portions and sulphuretted hydrogen was passed after each addition. When the reduction was over, the excess of alcohol was evaporated off on a water-bath and the solid mass was treated with a few c.c. of concentrated hydrochloric acid so as to form a paste. The paste was boiled with excess of water and then filtered from insoluble unchanged nitro compound. The filtrate on being rendered alkaline with ammonia gave yellow crystals of the amino compound. This was recrystallised from alcohol in fine needles, m.p. 143-45°. (Found: N, 8.4. $C_{13}H_7O_4N_2Br$ requires N, 8.3 per cent.).

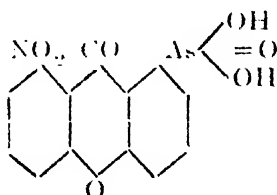
Introduction of Arsenic in Xanthenes.

3-Xantharsinic Acid.



3-Aminoxanthone (2.2 g.) was suspended in 20 c.c. of water and was dissolved by stirring in hydrochloric acid (2 c.c.). The solution was diazotised at 0° with a solution of sodium nitrite (0.8 g.) in water (5 c.c.) and was then introduced gradually in cooled mixture containing sodium carbonate (10 g.), arsenious oxide (4.5 g.), copper sulphate (0.3 g.) and water (25 c.c.), the whole being well stirred during the operation. The mass became reddish brown and nitrogen evolved and stirring was continued for 1 hour more. The reddish brown solution was concentrated and filtered. The filtrate was gradually acidified with hydrochloric acid till a small quantity of brown precipitate was produced. At this stage the mixture was filtered and the filtrate on further acidification gave a dull yellow precipitate. This was collected, redissolved in sodium bicarbonate, boiled with animal charcoal and filtered. The filtrate was then acidified when whitish yellow microcrystalline powder was obtained. The substance was found to be insoluble in most of the commoner organic solvents and hence the final purification was made by redissolving in sodium bicarbonate and reprecipitating it. It does neither melt nor shrink even upto 335°. (Found: As, 22.9. $C_{13}H_9O_5$ As requires As, 23.4 per cent.).

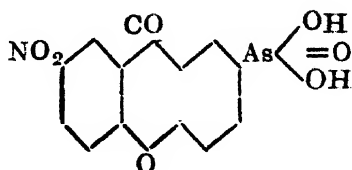
α-Nitroxantharsinic Acid.



This was prepared in a similar way as the previous compound by diazotising α -nitroaminoxanthone and adding the diazo solution to the arsenite solution. The resulting solution was of deep red colour and this on acidification gave at first a small quantity of scaly precipitate. At this stage the solution was again filtered and the filtrate on further acidification produced a brownish red product. The substance was observed to be readily soluble in alkalis and alkali carbonates and insoluble in most of the commoner organic solvents. Hence it was purified by dissolving in sodium carbonate, boiling the solution with animal charcoal, filtering and then reprecipitating with acid, when dull red microcrystalline product was obtained. It does

not melt even upto 330° , yield 60 p. c. (Found: As, 20.1. $C_{13}H_8O_7NAs$ requires As, 20.5 per cent.).

β -Nitroxantharsinic Acid.



The acid was prepared and purified in a similar way as the compound from β -nitroaminoxanthone. The substance dissolves readily in alkalis and alkali carbonates but is insoluble in most of the organic solvents. It does not melt even upto 340° , yield 65 p. c. (Found: As, 20.28. $C_{13}H_8O_7NAs$ requires As, 20.5 per cent.).

β -Aminoxantharsinic acid.—Ordinary ferrous sulphate (10.6 g.) was dissolved in warm water (35 c. c.) The solution was cooled well and was transferred to a wide-mouthed bottle fitted with a rubber stopper. This was treated with 25 p. c. solution of sodium hydroxide till the ferrous hydroxide mud reacted strongly alkaline to litmus paper on vigorous shaking. β -Nitroxantharsinic acid (3.5 g.) was dissolved in sodium hydroxide and this solution was poured at once into the hydroxide mixture, the whole being vigorously shaken for 5 minutes. The alkaline solution was allowed to stand for $\frac{1}{2}$ hour more and during this time the pale blue hydroxide gradually changed in colour to dark brown ferric hydroxide. The mud was separated by filtration through a large buckner funnel, the residue being finally washed with water. The filtrate was next acidified with concentrated hydrochloric acid whereby yellow amino compound was precipitated. This was crystallised from acetic acid. Does not melt even upto 347° . (Found: As, 22.1. $C_{13}H_{10}O_5NAs$ requires As, 22.3 per cent.).

β -Acetylaminoxantharsinic acid.—The sparingly soluble β -aminoxantharsinic acid was finely powdered and suspended in glacial acetic acid. To this excess of acetyl chloride was added and the mixture was heated under reflux for 2 hours. The hot reaction mixture was rapidly filtered and the filtrate was heated on a water-bath to expel the excess of acetyl chloride. The concentrated solution was then treated with cold water when the β -acetyl derivative separated out. The compound was filtered and then dried in a vacuum desiccator and it was finally crystallised as a yellow powder from acetic acid. The compound does neither melt nor shrink even up to 840° ,

yield 86 p. c. (Found: As, 19.5. $C_{15}H_{12}O_6NaAs$ requires As, 19.8 per cent.).

Bromonitrozantharsinic acid was prepared from monobromonitroaminoxanthone as before by the usual Bart reaction. The substance was purified by alternately dissolving in alkali and reprecipitating with dilute hydrochloric acid. The purified product is of cream coloured microcrystalline powder, m. p. 258-60° (decomp.). (Found: As, 16.57. $C_{13}H_7O_7NBrAs$ requires As, 16.8 per cent.).

Quinoline Derivatives.

3-Nitro-ψ-1:8-isonaphthoxazone.—3:6-Dinitrocoumarin (4 g.) was dissolved to a clear solution in concentrated sulphuric acid (7c. c.). To this solution glycerol (10 c. c.) was added, the addition of which caused the precipitation of the nitro compound with rise in temperature. This was stirred well and was allowed to cool to the room temperature. The cooled mixture was gradually heated in an oil-bath with constant stirring. The mass began to darken at 115° and a vigorous reaction took place between 138-40°. The vessel containing the reaction mixture was removed and allowed to cool with stirring. This was again heated on the bath to 120° and was kept at 135-40° for 1 hour. The temperature was next raised to 150-60° and allowed to remain at this for 5 hours. Finally the temperature was raised to 170° for $\frac{1}{2}$ hour. The black residue was finally powdered, repeatedly boiled with water and filtered after each time. The yellow filtrate was at first treated with concentrated ammonia and then with dilute ammonia whereby voluminous yellowish white precipitate was obtained. The addition of ammonia should be a gradual one as the substance is soluble in excess of the same. The precipitate was separated and then dried in a vacuum desiccator. It was crystallised from alcohol in colourless needles, m. p. 228-30°, yield 2.1 g. (Found: N, 11.48. $C_{12}H_6O_4N_2$ requires N, 11.57 per cent.).

8-Amino-ψ-1:8-isonaphthoxazone.—The nitro compound (5 g.) was dissolved by heating on a water-bath in alcohol. To the clear solution concentrated ammonia (20 c.c.) was added and sulphuretted hydrogen was passed in for 15 minutes. The addition of the latter substance at first gave a precipitate which dissolved to a yellow solution afterwards. The yellow solution was again heated and sulphu-

retted hydrogen passed after adding 20 c.c. more of ammonia. The reduction was complete when the solution assumed a brown coloration. The excess of alcohol was boiled off on a water-bath and concentrated hydrochloric acid was added to the residue so as to get a pasty mass. This was boiled with excess of water and filtered from the insoluble nitro compound. The filtrate was rendered alkaline whereby brownish yellow precipitate was obtained. The amino compound was crystallised from alcohol in light yellow fine needles, m. p. 270° , yield 30 p. c. (Found: N, 13.04. $C_{12}H_8O_2N_2$ requires N, 13.2 per cent.).

ψ -1:8-isonaphthoxazone-3-arsinic acid.—The amino compound described above was dissolved by heating in a solution of hydrochloric acid (1.5 c.c. in 10 c.c. water). The hot solution was rapidly cooled with ice so as to get the hydrochloride in a fine state of subdivision. To the well-cooled solution powdered ice was added and then a solution of sodium nitrite (0.5 g. in 5 c.c. water) was added at one time with stirring. The resulting diazo solution was gradually added with stirring to a well-cooled solution of sodium carbonate (6 g.), arsenious acid (2.5 g.), copper sulphate (0.2 g.) and water (30 c.c.). The addition of the diazo solution caused a slight frothing which subsided with time. The mass was stirred for $\frac{1}{2}$ hour more and was then allowed to stand for 1 hour at the room temperature. The yellowish brown solution was filtered from the suspended and insoluble substances and was next concentrated to a small bulk. Towards the end the whole was boiled for sometime with animal charcoal and filtered. The filtrate on cooling was acidified at first with concentrated and then with dilute hydrochloric acid when a brown precipitate of the arsinic acid derivative was obtained. The precipitate was separated and then dried in a vacuum desiccator. It was crystallised from acetic acid in cream coloured microcrystalline powder, m. p. $225-27^{\circ}$ (decomp.). (Found: As, 22.9. $C_{12}H_8O_5N$ As requires As, 23.3 per cent.).

β -Aminoxanthoquinoline was prepared by the reduction of nitroxanthoquinoline by sulphuretted hydrogen and ammonia in alcoholic solution. The substance was crystallised from alcohol in light crystals, m. p. $276-78^{\circ}$. (Found: N, 10.5. $C_{16}H_{10}O_2N_2$ requires N, 10.6 per cent.).

Xanthoquinoline- β -arsinic acid was prepared from *β -aminoxanthoquinoline* by subjecting it to Bart reaction. The acid thus obtained was purified by repeatedly dissolving in alkali and reprecipitating

with acid. This gave the substance as a light brown powder and was found to shrink at 315° but did not melt even up to 345° . (Found: As, 20.08. $C_{16}H_{10}O_5NaAs$ requires As, 20.2 per cent.).

In conclusion I take the opportunity of expressing my heartfelt thanks to Dr. M. Goswami, for his keen interest in this work and to the Director of Public Instruction, Bengal, for awarding me a Post-Graduate Research Scholarship which has enabled me to undertake the work.

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Studies on the Formation of Azoxy, Azo, Hydrazo and Benzidine Compounds and the Dyes Derived from the Latter.

By R. N. SEN AND R. SADASIVAM.

In the present work, the action of zinc dust and caustic soda, and zinc dust and ammonium chloride on aromatic nitro compounds has been further investigated with a view to study (a) the influence of the nature and position of the substituents on the formation of the azoxy, azo and hydrazo compounds and also on the subsequent benzidine transformation, and (b) the tinctorial properties of the dyes derived from the resulting benzidine compounds.

Reduction with caustic soda and zinc dust is now found to be very efficacious in the preparation of azo and hydrazo compounds from substituted nitrobenzenes *viz.*, *m*-nitrobenzoic acid, *m*- and *o*-nitrophenols, *m*- and *o*-nitrobenzaldehydes (*cf.* Loewenherz, *Ber.*, 1892, 25, 2795). In the case of the nitroaldehydes not only is the nitro group reduced, but the aldehydo group also undergoes reduction to the primary alcoholic group.

Comparing the yields obtained and the time of reduction of the nitro compounds to the hydrazo stage, it is found that the *meta* substituent influences the reduction more favourably than the *ortho*, although substitution in general retards the reduction of the nitro group. It is observed that the aldehydo group exerts the most and the phenolic group the least favourable influence on the formation of the hydrazo compounds.

The mixture of zinc and ammonium chloride, previously used by Cumming and Steel (*J. Chem. Soc.*, 1923, 123, 2464) for the reduction of α -nitronaphthalene to hydrazo and azo compounds, is found to be not suitable for the reduction of ordinary aromatic nitro compounds, although a heterocyclic nitro compound such as 6-nitrocoumarin is readily reduced yielding 60 per cent. azoxycoumarin and 30 per cent. aminocoumarin. 6-Nitrocoumarin is however completely reduced to

6-aminocoumarin by the action of zinc dust and caustic soda. Azoxycoumarin is very similar in properties to the azocoumarin synthesised by coupling diazotised 6-aminocoumarin with coumarin (Chakravarti, *J. Indian Chem. Soc.*, 1931, 8, 506). The solution of the compound in caustic soda undergoes geometrical inversion with mercuric oxide (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, 7, 247; Chakravarti, *ibid*, 1931, 8, 391). It is remarkable that azoxycoumarin on further reduction is converted wholly into aminocoumarin, no azo and hydrazo compounds being produced.

On the benzidine transformation of the hydrazo compounds studied, the position and the nature of the substituents appear to have a marked influence. It is found from the yield of benzidine derivatives from the hydrazo compounds investigated that of the groups OH, COOH, and CH₂OH, the OH group is most favourable for benzidine transformation while the CH₂OH group retards it. It is also observed that generally the *meta* substituent is more favourable for the benzidine transformation than the *ortho* substituent excepting the alcoholic group which when in the *meta* position does not exert any beneficial influence.

The new substituted benzidine compounds, prepared and described in this paper have also been tetrazotised, and the azo-dyes obtained from them by coupling with β -naphthol and β -naphthol sulphonic acid are substantive to cotton, while those obtained by coupling with dimethylaniline and β -naphthylamine behave like ordinary basic dyes. It is found that in all cases the azo-dyes derived from the *ortho* substituted derivatives produce deeper shades than the corresponding *meta* compounds. It is remarkable that even the *meta* compounds yield dyestuffs substantive to cotton which is not generally the case.

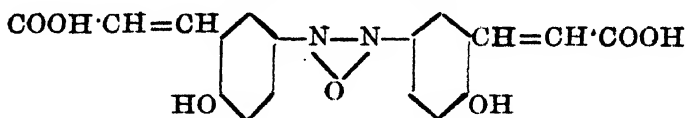
EXPERIMENTAL.

For the reduction of the nitro compounds to azo and hydrazo compounds with zinc dust, the mixture was mechanically stirred throughout the reaction. The stirrer passed through the inner tube of the condenser fitted to the flask containing the alcoholic solution of the nitro compound and zinc dust, caustic soda solution being added drop by drop from the top of the condenser. In the case of nitrocoumarin the zinc dust was slowly added through a second tube in the cork fitted to the flask, which was closed after each addition.

6-Azoxycoumarin.—6-Nitrocoumarin purified by crystallising from hot pyridine (10 g.) was mixed with alcohol (80 c.c.), ammonium

chloride (21 g.) and water (25 c.c.) added. Zinc dust (18 g.) was gradually added keeping the temperature between, 70-75°. In about 45 minutes the reaction was over. After cooling, the precipitated azoxycoumarin along with the zinc dust was filtered and washed repeatedly with boiling water to remove traces of aminocoumarin formed, which crystallised out from the filtrate. The mixture of the azoxycoumarin and zinc dust was treated in small quantities with dilute hydrochloric acid to remove the zinc dust. It crystallised from hot nitrobenzene as pale yellow clusters of thin long needles melting above 300°, yield 60 p.c. It is insoluble in most organic solvents except hot pyridine and and nitrobenzene. It is soluble in caustic soda solution with a deep orange colour, but is insoluble in ammonia, sodium carbonate or bicarbonate solutions. It dissolves in concentrated sulphuric acid with a red colour and is reprecipitated on dilution. (Found: N, 8.29. $C_{18}H_{10}O_5N_2$ requires N, 8.88 per cent.).

Azox-y-o-coumaric Acid.



Azoxycoumarin (1 g.) was dissolved in a 10 p. c. solution of caustic soda (20 c.c.) diluted with water (180 c.c.) and boiled for about $\frac{1}{2}$ hour with mercuric oxide (3 g.). The cold solution was filtered from mercuric oxide and acidified with hydrochloric acid. The gelatinous precipitate, thus obtained was washed with water, dissolved in ammonia, filtered and filtrate acidified, with dilute hydrochloric acid. The precipitate was crystallised from alcohol as a yellow microcrystalline powder decomposing above 270°. It decolourises bromine water and dilute potassium permanganate solution readily in the cold. It easily dissolves in alcohol, acetone, dilute ammonia, sodium carbonate and bicarbonate solutions. With concentrated hydrochloric acid its colour changes to deep violet. (Found: N, 7.7. $C_{18}H_{14}O_7N_2$ requires N, 7.78 per cent.).

The *diethyl ester*, prepared in the usual manner, crystallised from alcohol as a brownish yellow powder melting above 250°, yield 70 p. c. (Found: N, 6.6. $C_{32}H_{22}O_7N_2$ requires N, 6.56 per cent.).

m-Hydrazobenzoic acid.—To a mechanically stirred mixture of *m*-nitrobenzoic acid (9 g.) zinc dust (24 g.) and alcohol (20 c.c.), a solution of caustic soda (12 g.) in water (40 c.c.) was added drop by

drop in about 1 hour, keeping the temperature at about 90° . When the solution became colourless, it was filtered and the alcohol distilled off in an atmosphere of hydrogen. The solution was then filtered and treated with excess of dilute acetic acid and the precipitated *m*-hydrazobenzoic acid washed and dried, yield about 65 p.c. It was found identical with the compound obtained by Greiss (*Ber.*, 1874, 7, 1609) and by Strecker (*Annalen*, 1867, 141, 129) by different methods. (Found: N, 10.4. $C_{14}H_{12}O_4N_2$ requires N, 10.29 per cent.).

m-Diaminodiphenic acid.—The reduced alkaline solution containing the *m*-hydrazobenzoic acid was freed from zinc and boiled with excess of concentrated hydrochloric acid for a short time and left overnight. The precipitated dihydrochloride of *m*-diaminodiphenic acid was crystallised from hot water in white prisms from which the base itself was obtained as a microcrystalline solid by boiling with sodium acetate solution. It is easily soluble in caustic soda solution, sparingly in water and almost insoluble in dilute hydrochloric acid. (Found: N, 10.4. $C_{14}H_{12}O_4N_2$ requires N, 10.29 per cent.).

m-Dihydroxybenzidine.—This compound was obtained by reducing *m*-nitrophenol and subsequent benzidine transformation of the hydrazo compound thus formed in a similar way to the above. It crystallised from acetone in plates, m.p. 140° , and was found to be identical with the compound obtained by Elbs and Kirsch from *m*-azophenol (*J. pr. Chem.*, 1903, ii, 67, 265). (Found: N, 12.84. $C_{12}H_{12}O_2N_2$ requires N, 12.96 per cent.).

o-Hydrazophenol.—An alcoholic solution of *o*-nitrophenol was reduced as previously described with zinc dust and caustic soda until colourless. The solution was freed from zinc, the alcohol distilled off in an atmosphere of hydrogen, and the residue exactly neutralised with dilute acetic acid at 5° . The hydrazophenol that was precipitated along with zinc hydroxide was extracted with ether and the ether evaporated off in vacuum. It crystallised in colourless plates, m.p. 148° , yield 55 p.c. (approx.). It is soluble in hot water, alcohol, ether, dilute hydrochloric acid and dilute caustic soda solutions. It darkens on exposure and it gives a deep red coloration with ferric chloride. (Found: N, 12.8. $O_{12}H_{12}O_2N_2$ requires N, 12.96 per cent.).

Dibenzoyl derivative crystallised from chloroform as a brownish red microcrystalline powder, m.p. 186° . (Found: N, 6.47. $C_{26}H_{12}O_2N_4$ requires N, 6.6 per cent.).

o-Dihydroxybenzidine was prepared easily by directly treating the reduced solution after filtering off the zinc, with excess of concentrated hydrochloric acid at 0° and boiling the solution for a short time. On keeping overnight, the dihydrochloride crystallised as colourless plates. The free base was completely precipitated from aqueous hydrochloride solution with sodium carbonate. It crystallised from acetone in plates, m.p. 160°, yield 30 p.c. Hot water solution gives red precipitate with ferric chloride. It is soluble in dilute acids, caustic soda and sodium carbonate solutions, alcohol and acetone. (Found: N, 12·92. $C_{12}H_{12}O_2N_2$ requires N, 12·96 per cent.).

The dihydrochloride crystallised in colourless plates, m.p. 144°. (Found: Cl, 24·7. $C_{12}H_{14}O_2N_2Cl_2$ requires Cl, 24·5 per cent.).

Tetrabenzoyl derivative crystallised from chloroform as a microcrystalline powder, m.p. 180°. (Found: N, 4·24. $C_{40}H_{28}O_6N_2$ requires N, 4·4 per cent.).

Dibromo derivative was prepared by adding bromine water to a solution of *o*-dihydroxybenzidine in dilute hydrochloric acid. It crystallised from alcohol as a red microcrystalline powder, m.p. 174°. (Found: Br, 42·66. $C_{12}H_{10}O_2N_2Br_2$ requires Br, 42·78 per cent.).

Bismethylbenzoxazole was prepared by boiling *o*-dihydroxybenzidine with excess of acetic acid and fused sodium acetate for about 2 hours. The product was washed with acetic acid and crystallised from alcohol as glistening plates, m.p. 187°. (Found: N, 10·4. $C_{16}H_{14}O_2N_2$ requires, N, 10·6 per cent.).

o-Dihydroxybenzidinebisazo- β -naphthol.—A solution of *o*-dihydroxybenzidine was tetrazotised and coupled with an alkaline solution of β -naphthol, after keeping overnight the precipitated sodium salt was filtered and dried. It is a violet powder soluble in water and dyes cotton and wool to a pink shade. (Found: Na, 13·02. $C_{32}H_{20}O_4N_4Na_2$ requires Na, 13·26 per cent.).

It crystallised from alcohol as a reddish brown microcrystalline powder, m.p. 150°. (Found: N, 10·4. $C_{32}H_{22}O_4N_4$ requires N, 10·8 per cent.).

o-Dihydroxybenzidinebisazo- β -naphthol sulphonic acid (2:6).—Tetrazotised *o*-dihydroxybenzidine was coupled with a faintly alkaline solution of β -naphthol sulphonic acid. The reddish brown powder obtained on acidification, decomposes above 250° and dyes cotton and silk a pinkish shade. (Found: N, 8·12. $C_{32}H_{22}O_{10}N_4S_2$ requires N, 8·26 per cent.).

o-Dihydroxybenzidinebisazo- β -naphthylamine.—Tetrazotised *o*-dihydroxybenzidine was coupled with a solution of β -naphthylamine in acetic acid and the dye was precipitated with sodium acetate as an orange powder melting above 250° . It gives a deep orange solution in acetic acid. (Found: N, 16.12. $C_{32}H_{26}O_4N_6$ requires N, 15.96 per cent.).

o-Dihydroxybenzidinebisazodimethylaniline was prepared by coupling tetrazotised dihydroxybenzidine with dimethylaniline in glacial acetic acid. It was purified from alcohol, m.p. above 250° . (Found: N, 19.81. $C_{28}H_{32}O_2N_6$ requires N, 20.0 per cent.).

m-Azobenzyl alcohol.—A solution of *m*-nitrobenzaldehyde (10 g.) in alcohol (30 c.c.) was reduced at about 90° using zinc dust (18 g.) and a solution of caustic soda (14 g. in water 40 c.c.). In about 40 minutes the solution attained a very deep red colour, when the reduction was stopped and the alcohol distilled off. On cooling *m*-azobenzyl alcohol crystallised out. It recrystallised from hot water in orange yellow needles, m. p. 117° . It is freely soluble in alcohol and acetone and insoluble in benzene and ether. (Found: N, 11.44. $C_{14}H_{14}O_2N_2$ requires N, 11.57 per cent.).

The *diacetyl* derivative crystallised from acetone as a yellow microcrystalline powder. (Found: N, 7.2. $C_{28}H_{22}O_4N_2$ requires N, 7.05 per cent.).

m-Hydrazobenzyl alcohol.—*m*-Nitrobenzaldehyde was reduced as in the previous case until colourless. The hydrazo compound crystallised from pyridine, as a yellow microcrystalline powder, m. p. 268° , yield 75 p. c. It is sparingly soluble in alcohol but easily dissolves in sodium carbonate and caustic soda solutions. (Found: N, 11.4. $C_{14}H_{16}O_2N_2$ requires N, 11.51 per cent.).

The *diacetyl* derivative crystallised from alcohol as yellow microcrystalline powder decomposing above 220° . (Found: N, 8.84. $C_{18}H_{20}O_4N_2$ requires N, 8.56 per cent.).

The *dibenzoyl* derivative crystallised from chloroform as a crystalline yellow solid. (Found: N, 6.79. $C_{28}H_{24}O_4N_2$ requires N, 6.93 per cent.).

m-Dihydroxymethylbenzidine.—The reduced alkaline solution of above containing the hydrazobenzyl alcohol was freed from zinc and boiled with excess of concentrated hydrochloric acid for about 20 minutes; after 3 or 4 hours the solution was filtered and neutralised by the gradual addition of sodium hydroxide solution, when the *m*-dihydroxymethylbenzidine separated as a pale yellow precipitate.

The base was recrystallised from acetone as a white powder, m. p. 177° , yield 28 p. c. It is easily soluble in dilute acids and dilute caustic soda solution. (Found: N, 11.3. $C_{14}H_{16}O_2N_2$ requires N, 11.51 per cent.).

Tetrabenzoyl derivative crystallised from alcohol as microcrystalline powder, m. p. 233° . (Found: N, 3.13. $C_{42}H_{32}O_8N_2$ requires N, 3.23 per cent.).

Tetracetyl derivative, prepared by the usual method crystallised from alcohol as brown microcrystalline plate melting above 250° . (Found: N, 6.83. $C_{22}H_{24}O_6N_2$ requires N, 6.9 per cent.).

Dibromo derivative, prepared by adding bromine water to a solution of *m*-dihydroxymethylbenzidine in dilute hydrochloric acid, crystallised from alcohol as a deep brownish red microcrystalline powder melting above 270° . (Found: Br, 41.5. $C_{14}H_{14}O_2N_2Br_2$ requires Br, 41.8 per cent.).

m-Dihydroxymethylbenzidinebisazo- β -naphthol. — *m*-Dihydroxymethylbenzidine (2 g.) was tetrazotised and coupled with an alkaline solution of β -naphthol (2.95 g.). The azo-dye was purified from alcohol as a deep orange powder. It dyes silk a deep red shade from acetic acid bath. (Found: N, 10.4. $C_{34}H_{26}O_4N_4$ requires N, 10.1 per cent.).

m-Dihydroxymethylbenzidinebisazo- β -naphthol sulphonic acid (2:6) was prepared from tetrazotised *m*-dihydroxymethylbenzidine and β -naphthol sulphonic acid in the usual manner. It is a reddish brown powder which decomposes on heating. The aqueous solution dyes cotton and silk a deep red shade. (Found: N, 7.8. $C_{34}H_{24}O_4N_4S_2$ requires N, 7.7 per cent.).

m-Dihydroxymethylbenzidinebisazo- β -naphthylamine was prepared from *m*-dihydroxymethylbenzidine and purified from alcohol as an orange red powder, m. p. 120° . (Found: N, 14.1. $C_{34}H_{28}O_2N_6$ requires N, 14.4 per cent.).

m-Dihydroxymethylbenzidinebisazodimethylaniline, prepared from *m*-dihydroxymethylbenzidine and dimethylaniline, crystallised from alcohol as an orange microcrystalline powder, m. p. above 250° . It dissolves in acetic acid to a deep purple solution from which it dyes silk to a light orange shade. (Found: N, 16.57. $C_{30}H_{32}O_2N_6$ requires N, 16.5 per cent.).

o-Hydrazobenzyl alcohol. — The method adopted was the same as that in the case of *m*-hydrazobenzyl alcohol using *o*-nitrobenzaldehyde instead. The hydrazo stage was reached after 8 hours and the hydrazobenzyl alcohol crystallised from pyridine as a white microcrystalline powder.

talline powder, m. p. 200° , yield 70 p.c. It is easily soluble in sodium carbonate and sodium hydroxide solutions but is almost insoluble in alcohol or acetone. On boiling it with concentrated hydrochloric acid it is converted after about 10 minutes to *o*-dihydroxymethylbenzidine. (Found: N, 11.4. $C_{14}H_{16}O_2N_2$ requires N, 11.5 per cent.).

Diacetyl derivative crystallised from hot glacial acetic acid as soft needles, m.p. above 250° . (Found: N, 8.5. $C_{18}H_{20}O_4N_2$ requires N, 8.56 per cent.).

Dibenzoyl derivative crystallised from alcohol as a pale brown microcrystalline powder, m.p. 107° . (Found: N, 6.86. $C_{28}H_{24}O_4N_2$ requires N, 6.93 per cent.).

o-Dihydroxymethylbenzidine.—The procedure adopted was the same as in the case of the preparation of *m*-dihydroxymethylbenzidine but starting with *o*-nitrobenzaldehyde instead. It crystallised from acetone as a red microcrystalline powder, m.p. 185° , yield 40 p. c. It is soluble in alcohol, dilute acids and dilute caustic soda solution. (Found: N, 11.65. $C_{14}H_{16}O_2N_2$ requires N, 11.5 per cent.).

Tetrabenzoyl derivative crystallised from alcohol as a microcrystalline powder, m.p. above 250° . It is sparingly soluble in chloroform and insoluble in benzene. (Found: N, 3.1. $C_{42}H_{32}O_6N_2$ requires N, 3.23 per cent.).

Tetracetyl derivative crystallised from alcohol as a brown microcrystalline powder, m.p. above 250° . (Found: N, 6.88. $C_{22}H_{24}O_6N_2$ requires N 6.9 per cent.).

Dibromo derivative prepared by adding bromine water to a solution of the base in dilute hydrochloric acid crystallised from alcohol as a brown microcrystalline powder, m.p. above 250° . (Found: Br, 41.6. $C_{14}H_{14}O_2N_2Br_2$ requires Br, 41.8 per cent.).

o-Dihydroxymethylbenzidinebisazo- β -naphthol was prepared in a manner analogous to that of *m*-dihydroxymethylbenzidinebisazo- β -naphthol. It recrystallised from alcohol as a violet powder, m.p. above 250° . It dyes silk to a bluish violet shade from an acetic acid bath. (Found: N, 10.3. $C_{34}H_{26}O_4N_4$ requires N, 10.1 per cent.).

o-Dihydroxymethylbenzidinebisazo- β -naphthol sulphonic acid.—It was prepared similarly as dihydroxymethylbenzidinebisazo- β -naphthol sulphonic acid (2:6) but starting from *o*-dihydroxymethylbenzidine. It is a brownish red powder dissolving in water to a red solution from which it dyes cotton and silk to a red shade. (Found: N, 7.82. $C_{34}H_{24}O_4N_4S_2$ requires N 7.7 per cent.).

o-Dihydroxymethylbenzidinebisazo- β -naphthylamine, prepared from *o*-dihydroxymethylbenzidine (1.5 g.) and β -naphthylamine (2.2 g.) in the usual manner, crystallised from alcohol as a red microcrystalline powder, m.p. above 250°. It dissolves in glacial acetic acid to a reddish orange solution. It dyes silk a reddish orange shade from an acetic acid bath. (Found: N, 16.26. $C_{30}H_{32}O_2N_6$ requires N, 16.5 per cent.).

o-Dihydroxymethylbenzidinebisazodimethylaniline was prepared from tetrazotised *o*-dihydroxymethylbenzidine by coupling with an ice-cold solution of dimethylaniline and subsequent treatment with alkali. The compound was purified from alcohol as a dark coloured powder, m.p. above 250°. It dyes silk to a violet shade from an acid bath. (Found: N, 14.26. $C_{34}H_{28}N_6O_2$ requires N, 14.4 per cent.).

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Composition of Kapok Seeds.

By R. C. MALHOTRA.

Eriodendron anfractocum DC seeds were collected in September 1923 and 1925 from Java, Sumatra and the Malaya State Settlements. These were stored in tin cans after drying and were properly sealed. Within three months these were pulverised. Their oils were extracted for 28 hours with petroleum ether in Soxhlet apparatus. Various values of the oils were quantitatively determined, in triplicate, by the same procedure as used by Griffing and Alsberg (*Ind. Eng. Chem.*, 1931, 23, 908).

The data obtained from the above stated analysis is being presented below, which seem to indicate, that a definite and uniform composition of these seeds, as assumed by the above quoted authors, is not a universal phenomena. There are many factors which may modify their composition. It not only depends on the time of collection of seeds, the manner of their storage, the age and variety of the parent plant and the character of the soil on which it is grown, but also on the geographical position where the plant may have been located. Table shows the composition of the oils extracted from kapok seeds collected from various geographical positions.

	Griffing & Alsberg.	Obtained by the author.		
		Java.	Sumatra.	Malaya States.
Specific gravity at 25°	0.9225	0.9105	0.9216	0.9387
Refractive index	1.4691	1.4691	1.3810	1.5081
Saponification value	191.6	170.8	179.2	198.1
Iodine number (Hanus)	94.1	96.3	95.7	91.3
Acid value	9.65	Not determined		
Saturated acids (%)	17.15	18.90	17.85	19.60
Unsaturated acids (%)	76.32	75.98	76.56	75.00

This work was done while the author was in charge of the Biological Laboratories, Saint Marys, Kansas, U. S. A.

Review.

Quantitative Chemische Analyse—by Dr. C. A. Rojahn, fifth, fully revised edition, with 13 figures; P.XIV + 283. Published by Theodor Steinkopff, Dresden and Leipzig, 1931.

The present volume is a newly revised edition of Autenrieth's Quantitative Chemical Analysis. The book deals with the methods for the gravimetric estimation of metals, acids (anions), as well as with the important methods of their separation from one another. Analysis of typical minerals and silicates has also been included. All the different methods of volumetric analysis, such as acidimetry, alkalimetry, oxidation-reduction, iodimetry, precipitation, etc., have as well been fully dealt with. Methods for the analysis of certain pharmaceutical preparations, as well as of important technical products, like fats, oils, waxes, etc., have also been described. The chapter on water analysis deals fully with the subject though within a narrow compass. A short chapter is devoted on the analysis of phosphatic manures. The section on Colorimetry presents a special feature of the book, as it deals with most of the metals and important anions. The last chapter on electro-analysis furnishes all necessary informations on the subject, that might be required for everyday use in the laboratory. One, however, misses all informations about gas analysis, besides potentiometric and conductometric titrations. On the other hand, some of the older methods, which have been found to give unreliable results, have been retained without any justification. As an instance, mention can be made of the separation of Fe from Ni and Co by the basic acetate method. The same holds good also for the separation of Al from Ni and Zn.

Though all detailed theoretical considerations have been more or less avoided throughout the book, still, as a companion for daily use, it will be welcome in all chemical and pharmaceutical laboratories.

P. R.

The Oxidation of Sulphur Dioxide in the Electrodeless Discharge.

BY SAMPURAN DAS MAHANT.

Priestley ("Experiments and observations on different kinds of air," Birmingham, 1790, 2, 323) found that sulphur dioxide is decomposed by electric sparks. Buff and Hoffmann (*Annalen*, 1860, 113, 129) showed that sulphur and sulphur trioxide are formed by the sparking of sulphur dioxide and that sulphur trioxide is formed when a mixture of sulphur dioxide with half its volume of oxygen is exposed to the discharge. De Wilde (*Ber.*, 1874, 7, 256) and Poliakoff (*Mag. Chim. Cath. Katerinoslav.*, 1876, 27) obtained similar results with the silent electric discharge. Deville (*Bull. Soc. chim.*, 1865, 53, 366) stated that a state of equilibrium is reached which prevents the completion of the reaction, but that if sulphur trioxide is removed as fast as it is formed by absorption with concentrated sulphuric acid or water, the reaction may proceed to completion. Berthelot (*Ann. chim. Phys.*, 1898, vii, 14, 167, 289) said that some platinum sulphide may be formed on the platinum electrodes. According to Poliakoff the oxidation of sulphur dioxide is more or less completely dependent on the concentration, pressure, etc. If oxygen alone is subjected to the action of the discharge, it will unite with sulphur dioxide when removed from the influence of the discharge. Sulphur dioxide is, however, not so activated.

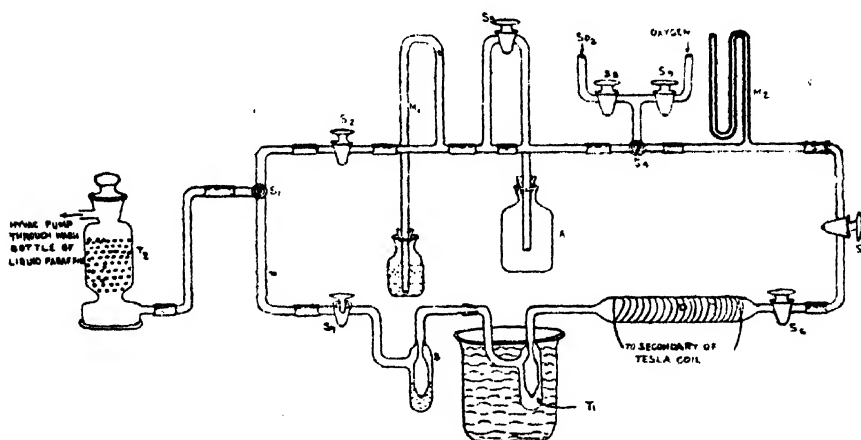
Henry and Wolf (*J. Phys. Radium*, 1929, 10, 81) believe that the emission spectrum of sulphur dioxide produced by an oscillating discharge is attributable to the production of sulphur monoxide.

The action of the electrodeless discharge in producing chemical changes has been the subject of investigation in these laboratories (Bhatnagar, Sharma and Mitra, *J. Indian Chem. Soc.*, 1928, 5, 879; Mahant, *ibid.*, 1929, 6, 705; Yajnik, Sharma and Bhatnagar, *Z. Phys. Chem.*, 1930, 148, 394) and the present communication

contains the results of a study of this source of excitation on the oxidation of sulphur dioxide.

EXPERIMENTAL.

The apparatus used in the present investigation is shown in the diagram. The aspirator A and the connecting tube upto stop-cock S_8 and S_9 were evacuated by connecting to the vacuum pump through the stop-cocks S_1 , S_2 , S_3 , and S_4 . Stop-cock S_2 was then closed and sulphur dioxide led into aspirator by opening the stop-cock S_8 , till the required pressure was indicated by the manometer M_1 . This was then closed and oxygen allowed to enter through the stop-cock S_9 till the manometer indicated no vacuum. Stop-cock S_3 was then closed and the gases allowed to diffuse into one another for 2 hours. The ratio of the gases in the mixture was calculated from the partial pressures as recorded by means of the manometer.



At the end of this interval, the discharge tube system was connected to the vacuum pump and evacuated. The mixture was then allowed to leak into the discharge tube through the stop-cock S_3 via the cocks S_4 , S_5 , and S_6 (the tube to S_8 and S_9 having been disconnected) while the discharge was allowed to pass for 5 hours. The rate of leakage of the gas into the system was regulated by means of the stop-cock S_3 . The mixture of gases was passed through a trap T_1 (immersed in ice) and then through a bubbler B containing a strong solution of caustic soda as it emerged out of the discharge tube. The pressure, at which the discharge was allowed to pass,

was 5-10 mm. and the system was evacuated from time to time to maintain this vacuum.

After the exposure the stop-cock S_3 was closed and S_2 loosened to allow air to sweep the tubes. The discharge tube was disconnected and well washed with water. The bubbler B was also well washed and both the washings mixed. The sulphite and sulphate contents were estimated and from this the percentage of oxidised sulphur dioxide was calculated.

The apparatus for the production of the electrodeless discharge has already been described (*cf.* Bhatnagar, Shrivastava, Mathur and Sharma, *Phil. Mag.*, 1928, **52**, 1226).

Preliminary investigations showed that only sulphate and sulphite were present in solution after exposure. No thionates could be detected except possibly in the case of pure sulphur dioxide when a yellowish precipitate was obtained with $Hg(NO_3)_2$ but no precipitate was obtained with $HgCl_2$ or $AgNO_3$ and no decolorisation could be noticed with $KMnO_4$. Free sulphur in a state of fine division was found to be sticking to the sides of the discharge tube when pure sulphur dioxide was subjected to the influence of the discharge and a drop of mercury in the discharge tube acquired a black coating of HgS . When the discharge was passed through a mixture of SO_2 and oxygen, a drop of mercury in the discharge tube formed a white coating which gave tests showing that a sulphate of mercury had formed.

Effect of the discharge on mixtures of different compositions.—Mixtures of different compositions were made by varying the ratio of the gases mixed in the aspirator and the effect of the discharge on these was studied. The results are given Table I.

TABLE I.

Composition ($SO_2 : O_2$)	...	50 : 50	60 : 40	70 : 30	80 : 20	100 : 0
SO_2 oxidised (%)	...	26.5	$\left\{ \begin{array}{l} 29.55 \\ 35.79 \\ 40.23 \end{array} \right.$	$\left\{ \begin{array}{l} 23.37 \\ 22.94 \\ 25.69 \end{array} \right.$	$\left\{ \begin{array}{l} 19.86 \\ 17.08 \\ 19.28 \end{array} \right.$	$\left\{ \begin{array}{l} 5.26 \\ 3.68 \\ 3.94 \end{array} \right.$

Influence of change of frequency on the percentage of sulphur dioxide oxidised.—The frequency of the oscillations from the secondary of the Tesla coil can be varied by varying the capacity in the circuit. To study the effect of change of frequency, the capacity in

the circuit was varied in the following way: In the first two experiments, two and four plates of the condenser were connected and in the last two experiments two and four plates from a similar condenser were connected in parallel with the 4 plates of the first condenser. A mixture of 60% SO_2 and 40% oxygen was used in this investigation. The results are given in Table II.

TABLE II.

No. of plates	2	4	6	8
Approx. capacity (microfarads)	22.4	67.2	89.6	134.4
SO_2 oxidised (%)	33.23	35.79	37.62	34.08

Influence of mercury.—During the course of the investigation mercury leaked into the discharge tube in some experiments in which the Hg seal stop-cock had been accidentally left loose. It was noticed in these cases that the percentage of sulphur dioxide oxidised was much greater. Careful analysis showed that though part of this increase was due to the precipitation of mercurous chloride along with the barium sulphate in the estimation, some of it was really due to some sort of catalytic effect of mercury. A regular investigation of this was undertaken and mixture of different compositions exposed to the discharge in the presence of mercury. The results are given in Table III.

TABLE III.

Composition ($\text{SO}_2 : \text{O}_2$) ...	60 : 40	70 : 30	80 : 20
SO_2 oxidised (%) ...	{ 46.53 51.11	{ 42.73 38.18	{ 30.57 36.82

Spectrographic study.—To elucidate the mechanism of the reaction, a spectral study of the discharge produced in the system was undertaken. The discharge tube employed for this purpose was the same as used for a study of oxygen in the electrodeless discharge and the arrangement of the apparatus altered to suit the requirements. Spectra of the glow produced in pure sulphur dioxide, sulphur dioxide in the presence of mercury, sulphur dioxide and oxygen as mixture, sulphur dioxide and oxygen in the presence of mercury, and of mercury in vacuum were taken on a Hilger E3 quartz spectrograph, Ilford special rapid panchromatic plates being used for photographing the spectra.

The mercury resonance line at 2536.7 \AA was not detected on the plates.

Discussion.

The results indicate that the maximum amount of sulphur dioxide is oxidised when the mixture has a composition of 60% sulphur dioxide and 40% oxygen. This may be compared to the 66% sulphur dioxide and 33% oxygen mixture which Buff and Hoffmann (*loc. cit.*) found was slowly converted into sulphur trioxide when subjected to the spark discharge. Coehen and Becker (*Z. Phys. Chem.*, 1919, **70**, 88) showed that on illumination by ultraviolet light the reaction $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$ is in equilibrium when about 100% of the sulphur trioxide has been formed, whereas in the light of a mercury lamp the equilibrium is reached when about 65% of the sulphur trioxide has been formed. They also showed that the equilibrium constant is independent of the proportions of sulphur dioxide and oxygen in the mixture and of the temperature.

The results on the influence of change of frequency do not show much change in the percentage of sulphur dioxide oxidised, the variations in the results being within the limits of experimental error. This is in agreement with the results of Hunt and Schumb (*J. Amer. Chem. Soc.*, 1930, **52**, 3152) on the effect of the electrodeless discharge on carbon dioxide. These authors did not find any appreciable variation in the percentage of decomposition when the wave-length of the discharge was changed from 51 to 34 metres.

Aqueous solutions of sulphur dioxide are known to be slowly oxidised to sulphuric acid with the precipitation of sulphur. Thiosulphuric and polythionic acids are also known to be formed in the course of the autoxidation. (*cf* Mellor, "Treatise on Inorganic and Theoretical Chemistry," London, Vol. X, p. 207). The absence of these thiosulphates and polythionates in the products of the reaction due to the electrodeless discharge shows that the mechanism of the process is not akin to autoxidation. According to Coehen (*Z. Electrochem.*, 1907, **21**, 545) the photochemical decomposition of sulphur dioxide furnishes sulphur and oxygen, the latter being largely used up to form sulphur trioxide. Hill (*Trans. Faraday Soc.*, 1924, **20**, 107) believes that the primary process involves either a dissociation of the sulphur dioxide molecule into atomic sulphur and molecular oxygen or simply an activation of the sulphur dioxide molecule so that the final result in either case is $3 \text{SO}_2 = 2 \text{SO}_3 + \text{S}$.

As already stated. Poliakoff (*loc. cit.*) has shown that if oxygen alone is subjected to the influence of the silent electric discharge, it will unite with sulphur dioxide even when removed from the influence of the discharge. Sulphur dioxide is however not so activated.

The general similarity of the spectra of the glow of sulphur dioxide and of mixtures of sulphur dioxide and oxygen shows that pure sulphur dioxide is first decomposed into oxygen and sulphur when subjected to the electrodeless discharge. The activated oxygen then combines with sulphur dioxide to give sulphur trioxide. In the case of mixtures of sulphur dioxide and oxygen, the oxygen alone is activated and combines with sulphur dioxide. It cannot be definitely said at present if the activation of oxygen is due to the formation of ozone or due to an activation of the molecule of oxygen as such. According to Hunt and Schumb (*loc. cit.*) there is no change of pressure when oxygen is exposed to the electrodeless discharge and hence no ozone is formed. This aspect of the question is under investigation and will be discussed in a separate communication.

The exact rôle of mercury in increasing the percentage of sulphur dioxide is also being investigated.

The thanks of the author are due to Prof. S. S. Bhatnagar, D.Sc., F. Inst. P., Director of the University Chemical Laboratories for his interest and guidance during the course of this investigation.

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Dyes Derived from Acenaphthenequinone. Part III.

Azines and Indigoid Vat Dyes.

By SISIR KUMAR GUHA.

This communication, which is an extension of the work of Sircar and Guha (*J. Chem. Soc.*, 1924, **125**, 335) and Guha (*ibid.*, 1931, 582), embodies the preparation of acenaphthaphenazines containing

the chromophoric group, $-N \begin{array}{c} \diagup O \\ \diagdown \end{array}$ in the "benzo"-ring of the molecule and a study of their properties. The azines obtained are 9-nitro-, 3-chloro-9-nitro-, 3-bromo-9-nitro-, and 3:4:9-trinitroacenaphthaphenazines. All these coloured bodies are characterised by their very sparing solubility in alcohol. Although very stable they volatilise without decomposition when heated strongly above their melting points yielding coloured vapours of the respective substances which deposit again as pure dyes. The first three compounds dye wool a shade of lemon-yellow and the last named produces a deep yellow shade from an acid bath when freshly precipitated by water from strong sulphuric acid solution.

9-Aminoacenaphthaphenazine has also been obtained from the corresponding nitro compound by reduction (*cf.* Heckendorn, *Helv. Chim. Acta*, 1929, **12**, 50). The identity of the compound was established by the preparation of the same aminoazine from acenaphthenequinone and reduced chrysoidine (*cf.* Witt, *J. Chem. Soc.*, 1886, **49**, 401). It dyes wool in bright yellow shades from an acid bath which is fast to alkali and acid but not to light.

The following table shows that the dyeing shades of some of the azines mentioned are in no way inferior to those of the corresponding phenanthraquinone derivatives (Heim, *Ber.*, 1888, **21**, 2305; Witt, *loc. cit.*).

Compound.	Dyeing shade on wool.
9-Nitroacenaphthaphenazine	Lemon yellow
Nitrophenanthraphenazine	" "
9-Aminoacenaphthaphenazine	Bright "
Aminophenanthraphenazine	" "

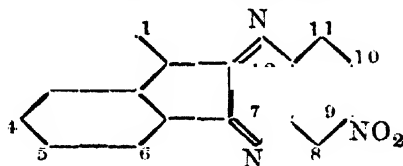
Finally, three derivatives of 2-thionaphtheneacenaphthylene-indigo, commercially known as Ciba scarlet G (Hezdzik and Friedlander, *Monatsh.*, 1908 **29**, 306; Grob, *Ber.*, 1908, **41**, 3331; E. P. 34408; A. P. 891690 containing Cl, Br and NO₂ respectively in the

acenaphthene part of the molecule, have been prepared*. These substances bear resemblance to azines exhibiting their distinctive sulphuric acid reaction. Further, they behave similarly to nitroazines (*loc. cit.*), when heated above their melting points. Alkaline hydrosulphite forms a coloured vat with each of these compounds from which the dye can be reprecipitated by treatment with air. The dyed shades are quite even and fast. These dyes were also found quite suitable for dyeing on wool from an acid bath when freshly precipitated unchanged from strong sulphuric acid solution by water.

A comparison of the scarlet red shade obtained from the chloro- and bromoindigoid derivatives on cotton as well as on wool with that of the same shade of Ciba scarlet G (prepared for the purpose) on same medium, exhibits that notwithstanding the decisive redder shades of the former two compounds, brilliancy and glazy pleasantness are prominent in the shade of the latter, the mother compound. Work in this line is in progress.

EXPERIMENTAL.

9-Nitroacenaphthaphenazine.



The crystalline yellow precipitate, produced by bringing together acenaphthenequinone (0.72 g.) and 4-nitro-*o*-phenylenediamine (0.61 g.) in 50 c. c. of boiling glacial acetic acid, after being purified by boiling successively with a small quantity of alcohol and acetic acid in which the condensation product was only sparingly solution separated from pyridine in beautiful lemon yellow prisms or from aniline in thin square plates, m.p. above 310°. It is soluble in aniline or pyridine, sparingly soluble in chloroform, benzene, or amyl alcohol and insoluble in caustic alkalis, ammonia or ether. It dissolves in strong sulphuric acid with a reddish brown colour and when reprecipitated by water dyes wool in lemon-yellow shades from an acid bath. (Found: N, 18.99. $C_{18}H_9O_2N_3$ requires N, 14.04 per cent.).

* In German patent 282170 halogenated derivatives of Ciba scarlet G, obtained by condensing thioindoxyl with halogen derivatives of acenaphthenequinone have been described. Editor.

3-Chloro-9-nitroacenaphthaphenazine separated in lemon-yellow clusters of needles during heating 3-chloroacenaphthenequinone (0.43 g.) and 4-nitro-*o*-phenylenediamine (0.31 g.) in 40 c.c. of boiling glacial acetic acid for 15 minutes. It was first boiled with alcohol and then for sometime with a little acetic acid. The residue recrystallised from acetic in lemon-yellow needles, m.p. 287° (shrinking previously at 284°). It is soluble in benzene, chloroform, acetic acid, pyridine or amyl alcohol, sparingly soluble in alcohol or acetone. The substance gives a deep reddish brown solution with concentrated sulphuric acid and dyes wool in lemon-yellow shades from an acid bath. (Found: Cl, 10.26. $C_{18}H_8O_2N_3Cl$ requires Cl, 10.64 per cent.).

3-Bromo-9-nitroacenaphthaphenazine was similarly obtained in rectangular crystalline precipitate from 3-bromoacenaphthenequinone (0.52 g.) and the diamine (0.31 g.) in 53 c.c. of boiling glacial acetic acid and crystallised from pyridine in fine lemon-yellow needles, m.p. 295°. It is similar in appearance and in solubility to the preceding compound and dyes wool in lemon-yellow shades from an acid bath. (Found: Br, 21.39. $C_{18}H_8O_2N_3Br$ requires Br, 21.16 per cent.).

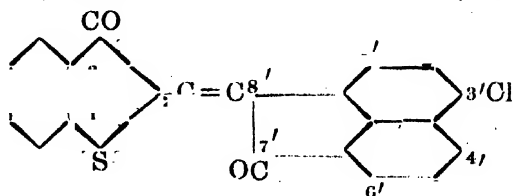
3:4:9-Trinitroacenaphthaphenazine.—A solution of 4-nitro-*o*-phenylenediamine (0.31 g.) in hot glacial acetic acid (16 c.c.) was added to the solution of powdered 3:4-dinitroacenaphthenequinone (0.54 g.) in 70 c.c. of boiling glacial acetic acid and the mixture kept boiling for 20 minutes. The resulting yellowish brown liquid when cooled, separated the condensation product in deep yellow rectangular plates which after being purified by boiling with alcohol recrystallised from moderately strong acetic acid. The azine melts at 300-1°, and gives a light yellow solution in concentrated sulphuric acid and dyes wool in deep yellow shades from an acid bath. It is soluble in benzene, chloroform, acetone, acetic acid, pyridine or aniline, sparingly soluble in alcohol, ligroin or amyl alcohol. (Found: N, 18.12. $C_{18}H_7O_6N_5$ requires N, 17.99 per cent.).

9-Aminoacenaphthaphenazine.—(i) 9-Nitroacenaphthaphenazine (1 g.) suspended in absolute alcohol (60 c.c.) was reduced by stannous chloride (4 g.) and concentrated hydrochloric acid (6 c.c.). The mixture was boiled on the water-bath with occasional shaking. It first turned pink-red and then to dark magenta-red and finally violet coloured precipitate of the hydrochloride of the base separated in $1\frac{1}{4}$ – $1\frac{1}{2}$ hours. Water (180 c.c.) was added to the reaction mixture and the whole warmed, filtered, and the alcohol distilled off. The

dark magenta-red solution on treatment with strong ammonia slowly separated the aminoazine in deep yellow flakes. This was collected and further purified by dissolving in a little cold dilute hydrochloric acid (2N approx.) and excess of cold water and liberating the base again by the addition of ammonia. It was finally crystallised from xylene or in better yield from aniline in silky rectangular prisms. The crystals were thoroughly washed with cold dilute acetic acid (2N approx.) and boiling water. It does not melt below 310° . Concentrated sulphuric acid dissolves it with an orange-red coloration and it dyes wool in bright yellow shades from an acid bath. It is readily soluble in chloroform, acetone, alcohol, amyl alcohol, pyridine or aniline, moderately soluble in benzene or ether. It dissolves in cold glacial acetic acid yielding reddish brown solution from which the base can be reprecipitated by the addition of alkalis. It is insoluble in cold dilute acetic acid. (Found: N, 15.64. $C_{18}H_{11}N_3$ requires N, 15.61 per cent.).

(ii) *Second method*.—Powdered chrysoidine hydrochloride (1.8 g.), dissolved in hot glacial acetic acid (55 c.c.) was reduced by gradually adding zinc dust (9–10 g.). The colourless filtered solution was added to the solution of acenaphthenequinone (1 g.) in 55 c.c. of glacial acetic acid and the mixture boiled for 2–3 minutes. On adding powdered anhydrous sodium carbonate to the cooled deep brown solution and stirring, a pasty mass was obtained. This was treated with water (250 c.c.) and the separated brown amorphous precipitate filtered, and washed with hot water. It was purified in the same way as in the first method and found to be identical with the preceding aminoazine. (Found: N, 15.39. $C_{18}H_{11}N_3$ requires N, 15.61 per cent.).

2-Thionaphthene-8' (3'-chloro) acenaphthylene-indigo.



3-Chloroacenaphthenequinone (0.64 g.) in boiling glacial acetic acid (25 c.c.) was treated with concentrated hydrochloric acid (1 c.c.) and to this mixture a solution of 3-hydroxythionaphthene (0.45 g.) in 25 c.c. of hot glacial acetic acid added. The mixture was heated on the water-bath at $80-85^{\circ}$ for 10 minutes when deep scarlet

red needle shaped crystals separated. These were filtered, washed with acetic acid and hot water. For further purification it was successively boiled with a little alcohol and acetic acid and finally crystallised from acetic acid, pyridine or amyl alcohol in scarlet red needles, m. p. 280° . It is soluble in benzene, chloroform, xylene, pyridine, aniline, amyl alcohol or acetic acid and sparingly soluble in acetone, alcohol or ligroin. Strong sulphuric acid dissolves it with a deep green solution from which water reprecipitates the original substance which dyes wool from an acid bath in scarlet red shade. With alkaline hydrosulphite it gives a bluish violet vat by which cotton is coloured scarlet red when exposed to atmospheric oxygen. (Found: Cl, 10.54. $C_2H_9O_2ClS$ requires Cl, 10.18 per cent.).

2-Thionaphthene-8th (3'-bromo)-acenaphthylene-indigo was prepared from 3-bromoacenaphthenequinone (0.52 g.) and 3-hydroxythionaphthene (0.3 g.) in the same way as and possesses properties similar to the preceding compound, m. p. 287° . (Found: Br, 20.21. $C_{20}H_9O_2BrS$ requires Br, 20.35 per cent.).

2-Thionaphthene-8th (3':4'-dinitro)-acenaphthylene-indigo. — The solutions of 3:4-dinitroacenaphthenequinone (0.27 g.) in 50 c.c. of glacial acetic acid and 3-hydroxythionaphthene (0.15 g.) in 30 c.c. of glacial acetic acid were made free from dissolved air by passing dry carbon dioxide for 5 minutes and mixed together and 5 c.c. of concentrated hydrochloric acid added. The mixture was boiled for 5-6 minutes by which time dark red crystalline precipitate separated. This was filtered at once, washed first with acetic acid and then with hot water. After being boiled with alcohol it was crystallised from pyridine in hexagonal prisms, not melting below 300° . It is soluble in pyridine or xylene, moderately soluble in chloroform or benzene and sparingly soluble in alcohol, amyl alcohol, or acetic acid. It dissolves in strong sulphuric acid giving a blackish brown solution and dyes wool in dark red shades from an acid bath. The vat formed by the action of the alkaline hydrosulphite on this dye is yellow-brown and on exposure to air the dark red colouring matter is regenerated on cotton fibre. (Found: N, 6.75. $C_{20}H_8O_6N_2S$ requires N, 6.93 per cent.).

I avail myself of this opportunity to express my thanks to Dr. K.S. Caldwell, Principal, Science College, for his interest during the progress of the work.

Actinodaphnine. An Alkaloid from *Actinodaphne hookeri*, Meissn.

By S. KRISHNA AND T. P. GHOSE.

Actinodaphne, vern., *Pisi* (Bomb.) " belongs to a genus of trees or bushes (N. O. *Laurineae*) comprising of about 50 species of which 9 or 10 are Indian, inhabiting the warm, moist forests of the lower hills. It is found common in eastern and western Ghats of S. India and in Kanara and particularly in Mahabaleshwar. A cold infusion of the leaves is mucilaginous and is used in urinary disorders and in diabetes" (Dymock). Allied to *Actinodaphne* are the *Litsea* species and the best known of which is *Litsea sebifera*, vern., *Maidalakri* (Hind.). It is a very popular Indian drug and from its bark an alkaloid has been isolated which is identical with laurotetanine, an alkaloid, isolated by N. Greshoff from three species of Java *Litsea* (Ber., 1890, 23, 3537). This is also said to be present in several other plants belonging to the N. O. *Laurineae*.

The present work was undertaken to find if laurotetanine was the principal active constituent of *Actinodaphne hookeri*, which is reputed in Ayurvedic system of medicine to be efficacious in diabetic diseases. And for this purpose the bark of the tree was extracted in the usual manner which yielded about 0.7 per cent. of an alkaloid and the pure product from this was obtained on repeated crystallisation from suitable solvents, as it was only in this manner that the last traces of the colouring matter were possible to remove. The alkaloid crystallises in stout prisms, m.p. 210–11°. The analytical data, molecular weight, equivalent weight, etc., all tend to indicate for the alkaloid the formula $C_{18}H_{19}O_4N$ and a molecular weight of 313. It has been found to contain a hydroxyl, a methoxyl and a N-methyl group. Possibilities of a second hydroxyl and methoxyl group have also been explored but with negative results. The alkaloid gives no oxime or a phenylhydrazone and therefore, the absence of an aldehydic or carbonyl grouping is strongly suspected. From these it appears that the alkaloid from *Actinodaphne hookeri* bark is quite different from laurotetanine which contains three

methoxyl and one hydroxyl group. It is, therefore, proposed to designate this alkaloid as *Actinodaphnine*.

There appears to be a certain similarity between actinodaphnine and bebeerine, an alkaloid found in the bark of *Nectandra rodiaci* and *Herandia sonora* (N. O. *Laurineae*). Bebeerine crystallises from methyl alcohol in small prisms, m.p. 214°. It is soluble in alkalis. It has a formula of $C_{18}H_{21}O_3N$; it is a tertiary base containing one methoxyl, one hydroxyl and one N-methyl group, but in the physical data of its salts it is quite different to those of actinodaphnine (Scholtz, *Arch. Pharm.*, 1898, **236**, 530).

The leaves of *Actinodaphne hookeri* were also examined and a dark brown amorphous base was isolated but the quantity was too small for proper identification. The alkaloid forms amorphous salts and has been found to possess an acid equivalent of 487. The salts of actinodaphnine, on the other hand, are all easily crystallisable and from this it appears that the leaves contain a different alkaloid from that contained in the bark of the tree.

EXPERIMENTAL.

Extraction of the alkaloid from the bark.—Various methods were tried for extraction of the alkaloid with a view to getting the best yield and the one finally adopted is as follows: 500 G. of the finely powdered bark (containing 9 p. c. moisture) was mixed with sodium carbonate (200 g.), triturated with a little water (100 g.) and extracted with 90 p. c. alcohol by cold percolation till the alcohol was colourless. The alcohol from the extract was completely removed by distillation under reduced pressure and the residue extracted several times with 3 p. c. acetic acid. The colouring matter from the extract was removed by precipitation with lead acetate and after removal of the excess of lead acetate and sulphuretted hydrogen in the usual manner, the alkaloid was precipitated with ammonia. If at this stage the acid liquors are still coloured, the same can be removed by treatment with animal charcoal. The precipitated base was extracted with excess of ether which dissolved the base but very little of the colouring matter. The ethereal extract on drying over anhydrous magnesium sulphate was distilled to remove the solvent when the alkaloid was left behind as a white crystalline powder in a yield of about 0.7 p. c. The usual chloroform-ether extraction gave only 0.5 p. c. yield. This

procedure has an additional disadvantage in that the alkaloid could never be completely freed from the colouring matter when chloroform was employed for extraction.

The crude alkaloid, obtained in the above manner, was crystallised from acetone containing a little water and the crystals so formed were dried in air on a porous tile melting at $206-7^{\circ}$. These still retained some colouring matter which was possible to remove only on crystallisation from benzene, and on final crystallisation from absolute alcohol the alkaloid was obtained in prismatic needles, m.p. $210^{\circ}-11^{\circ}$. (Found: C, 68.8; H, 5.8; N, 4.3; M. W., 310 (Rast). $C_{18}H_{19}O_4N$ requires C, 69.0; H, 6.1; N, 4.5 per cent.; M. W., 313).

Actinodaphnine is *dextrorotatory*, $[\alpha]_D^{20} = +32.77^{\circ}$ in absolute alcohol. It does not contain any water of crystallisation as its weight and melting point remain unaltered on drying at 105° for several hours. It is almost insoluble in water but dissolves freely in alcohol, acetone, chloroform, and benzene and is sparingly soluble in ether. In most of the solvents it shows a pale blue fluorescence. On exposure to light it darkens. It dissolves in caustic alkalis from which it is recovered unchanged but it is insoluble in sodium carbonate. It dissolves in concentrated sulphuric acid with a beautiful pink colour which on standing deepens to purple and on warming to reddish brown or black. In cold concentrated sulphuric acid containing traces of dichromate or nitric acid it develops a deep blue colour while with nitric acid alone it forms a deep yellowish brown colour. Aqueous solution of its hydrochloride gives a reddish brown coloration with dilute ferric chloride solution.

Actinodaphnine hydrochloride was obtained by dissolving the base in alcohol and adding alcoholic acid. On addition of ether to the above mixture and standing, the hydrochloride crystallised out in needles and these on twice recrystallisation from alcohol and ether gave fine silky needles, m. p. $280-81^{\circ}$ with frothing and decomposition. (Found: HCl, 10.15. $C_{18}H_{19}O_4N$, HCl requires HCl, 10.3 per cent.). It is only moderately soluble in cold water and its aqueous solution is *dextrorotatory*, $[\alpha]_D^{20} = +8^{\circ}-45'$. The hydrochloride when prepared and crystallised from aqueous solution and dried in air melts at 280° and no water of crystallisation was found even when kept at 105° for a few hours.

Hydroiodide was prepared by suspending the base in methyl alcohol and adding hydroiodic acid, also dissolved in methyl alcohol,

till just faintly acidic. On addition of ether to form opalescence and on standing stout prismatic needles separated which on recrystallisation from alcohol melted at $264-65^{\circ}$ with frothing and decomposition. (Found: HI, 29.3. $C_{18}H_{19}O_4N$, HI requires HI, 29.0 per cent.).

Sulphate.—The base was suspended in water and dilute sulphuric acid added till just acidic. The sulphate rapidly crystallised out in fine silky needles from the solution in which it is only moderately soluble. Recrystallisation from dilute alcohol gave colourless silky needles which turn yellow or brown on keeping in evacuated desiccator. The sulphate contains 3 molecules of water of crystallisation. The dried salt melts at $249-50^{\circ}$ (decomp.). [Found: H_2SO_4 , 13.7. $(C_{18}H_{19}O_4N)_2 \cdot H_2SO_4$ requires H_2SO_4 , 13.3 per cent.].

Picrate was prepared in the usual manner and on recrystallisation from dilute alcohol separated in fine silky needles, containing one molecule of water of crystallisation. The dried salt decomposes at $220-22^{\circ}$ without melting.

Methiodide was obtained by refluxing on a water-bath a mixture of the base (2 g.) in methyl alcohol (60 c.c.) and methyl iodide (4 g.). On removal of the solvent the methiodide separated as brown silky needles and on recrystallisation from alcohol-ether mixture, melted at $243-44^{\circ}$. (Found: CH_3I , 31.4. $C_{18}H_{19}O_4N$, CH_3I requires CH_3I , 31.2 per cent.).

Methoxyl group was determined by Perkin's modification of Zeisels method (*J. Chem. Soc.*, 1903, 83, 1367). (Found: OCH_3 , 13.9. $C_{18}H_{19}O_4N$ requires OCH_3 , 9.9 per cent.). The results for methoxyl group were intermediate between the values calculated for one and two methoxyl group and is slightly less than that required for one methoxyl and one N-methyl group and from this it appears that the alkaloid contains one OCH_3 and one NCH_3 group which partially decomposes to give the higher values for OCH_3 .

Hydroxyl group.—Actinodaphnine could not be acetylated by direct treatment with acetyl chloride as in the case of laurotetanine (Filepe, *Arch. Pharm.*, 1898, 236, 601). It was, therefore, acetylated by heating 2 g. of the base dissolved in excess of acetic anhydride on a water-bath at $70^{\circ}-75^{\circ}$. After about 3 hours heating the solution was poured in water when the acetylated product precipitated as a white powder. This was collected, dried and recrystallised from ethyl acetate as light brown tufts of prisms. Dried at 105° it melted at $229-80^{\circ}$. (Found: C, 67.9; H, 5.5. $C_{18}H_{18}O_3N \cdot OAc$)

requires C, 67.6 ; H, 5.9 per cent.). The acetylated product (dry) was hydrolysed with $N/2$ alcoholic potash, on a waterbath for 1 hour. (Found: OAc, 155.7. $C_{18}H_{18}O_3N \cdot OAc$ requires, 157.7).

Benzoylation was conducted in the usual manner by treating the base (2 g.) with benzoyl chloride (12 c.c.). The product when crystallised from alcohol and ethyl acetate, was obtained as light yellow plates, m.p. 232—33°.

Summary.

1. From the bark of *Actinodaphne hookeri* a new alkaloid has been isolated which is different from the alkaloids, laurotetanine, bebeerine and buxine found in certain plants of the N. O. *Laurineae*. The new alkaloid has been designated as actinodaphnine.

2. The preliminary examination shows it to possess the formula $C_{18}H_{19}O_4N$, Mol. wt. 313 and contain a methoxyl, a N-methyl and a hydroxyl group.

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DEHRA DUN, U. P.

Received August 10, 1932.

**The Directive Effect of Substituents on the Cyclisation
of Substituted *s*-Diarylthiocarbamides. Part I.
The Effect of Fluoro, Iodo, and Cyano Substituents
on the Formation of Anilinobenzthiazole
Derivatives from Mono-*p*-substituted
Thiocarbanilides and Bromine.**

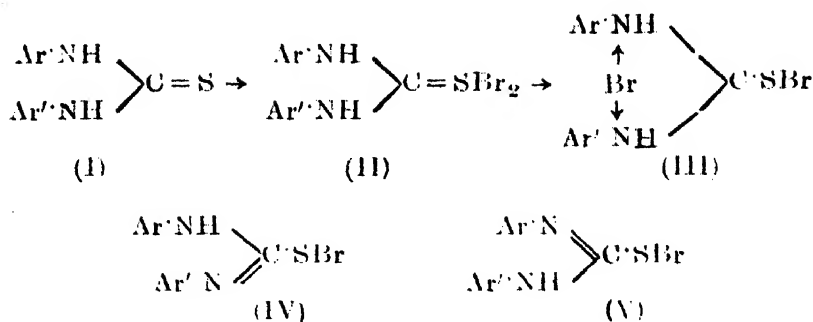
BY ROBERT FERGUS HUNTER.

The object of the investigation of which this is Part I. is to study the effect of different substituents and hydrocarbon groupings on the thiazole cyclisation of *s*-diarylthiocarbamides by bromine and other reagents.

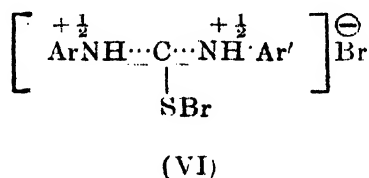
Before embarking on a discussion of the effect of substituents on the cyclisation of thiocarbanilides by bromine, it is necessary to explain our view of the mechanism of the transformation. Since Lecher's experiments on the oxidation of tetrasubstituted thiocarbamides to disulphide derivatives (*Annalen*, 1925, **445**, 35) have invalidated all the classical arguments in favour of the formula $\text{NH}_2\cdot\text{C}(\text{SH})\cdot\text{NH}$ for thiocarbamide, and the X-ray analysis of this compound (Hendricks, *J. Amer. Chem. Soc.*, 1928, **50**, 2455) indicates that it has the thioamide structure, $\text{CS}(\text{NH}_2)_2$, in the crystalline condition, it is evident that the salts of thiocarbamides (Dixon, *J. Chem. Soc.*, 1917, **111**, 318) should be written $\left[(\text{NH}_2)_2\text{C}=\overset{\oplus}{\text{S}}\text{H} \right] \overset{\ominus}{\text{X}}$, and are clearly the reactive units in the well known oxidation experiments already referred to.

It may therefore be assumed that a diarylthiocarbamide will normally be present in solution in an inert solvent such as chloroform, in the thioamide phase (I). The first action of bromine would therefore be expected to result in the formation of a dibromide (II), in which bromine may subsequently migrate as ion to the nitrogen atoms, yielding the salt (III), which can give rise to either of the tautomerides (IV) or (V) by incipient loosening of

hydrogen bromide (Hunter and Jones, *J. Chem. Soc.*, 1930, 2190).

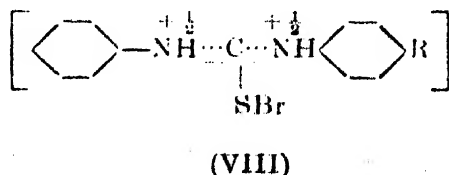
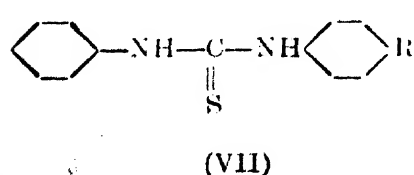


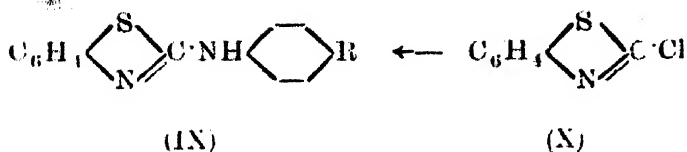
Recombination of the eliminated hydrogen bromide with the amidines (IV) and (V) will, however, result in the production of a common ammonium ion (VI) (Birtles and Pyman, *J. Chem. Soc.*, 1923, 123, 362), in which it may be assumed that the charge is located to the extent of approximately a half positive charge on each nitrogen atom (compare Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147).



Elimination of bromine from the bromothiol grouping in this along with the *ortho* hydrogen atom of the aromatic nucleus on which ring formation takes place, then yields the hydrobromide, or hydropromide, of the anilinobenzthiazole.

The effect of a substituent R, on the direction of cyclisation of a substituted thiocarbanilide (VII), may therefore be assumed to depend on its relative effect on the reactivity of the hydrogen atoms attached to the nuclear carbon atoms which are *ortho* to the nitrogen atoms in the amidine ion (VIII).





It has previously been shown that the bromination of *p*-chloro- and *p*-bromo-*s*-diphenylthiocarbamides (VII, R=Cl and Br) gives rise to 4'-substituted-1-anilinobenzthiazoles (IX) (Dyson, Hunter, and Soyka, *J. Chem. Soc.*, 1929, 458). As might therefore be anticipated, it has been found that ring formation occurs on the unsubstituted nucleus when *p*-fluoro- and *p*-iodo-*s*-diphenylthiocarbamide (VII, R=F and I) are treated with bromine under the usual conditions, with the production of the corresponding 4'-substituted-1-anilinobenzthiazoles (IX, R=F and I), whose formulae are established by their synthesis from 1-chlorobenzthiazole (X) and the corresponding *p*-halogenoanilines.

Particular interest attaches itself to the effect of the cyano group in view of the *meta* directive property of triple linkages in aromatic substitution, which has been attributed (Baker, Cooper, and Ingold, *J. Chem. Soc.*, 1928, 426) to the tendency of a system of six electrons which are mutually shared by two atomic nuclei, to attract additional electrons in order to form a stable association of eight, or if possible, ten electrons. This can be represented symbolically in the case of hydrocyanic acid as $\text{H}-\text{C} \equiv \text{N}$, and provides an explanation for the acidity of this compound and for the non-basicity of the nitriles.

As might be anticipated from this, the cyano group in *p*-cyano-*s*-diphenylthiocarbamide causes cyclisation to take place on the unsubstituted nucleus on treatment with bromine, with the production of 4'-cyano-1-anilinobenzthiazole (IX, R=CN).

The fact that this group, and the strongly *meta* directing nitro group (Hunter and Jones, *loc. cit.*) do not favour cyclisation on the nucleus opposite to that involved in the case of thiocarbanilides containing *o*-*p*-directive substituents, is due to the fact that *meta*-substitution is essentially a residual effect produced by the disappearance of free affinity from the *o*-*p*-positions in an aromatic nucleus (compare Ingold, *Annual Reports of the Chem. Soc.*, 1926, 184).

EXPERIMENTAL.

p-Fluoro-*s*-diphenylthiocarbamide.—A solution of *p*-fluoroaniline (0·7 c.c.) in absolute alcohol (5 c.c.) was added to phenylthiocarbamide (0·8 c.c., dissolved in 5 c.c. of the same solvent) and the mixture was heated for a short time and then concentrated on a water-bath. On recrystallisation from alcohol the *thiocarbamide* was obtained in glistening plates, m.p. 175-76°. (Found: S, 13·0. $C_{13}H_{11}N_2FS$ requires S, 13·0 per cent.).

4'-Fluoro-1-anilinobenzthiazole (IX, R=F). (i) *The action of bromine on p*-fluoro-*s*-diphenylthiocarbamide.—A suspension of the thiocarbamide (0·7 g.) in chloroform (8 c.c.) was treated with bromine (0·9 c.c. in 1 c. c. of chloroform) and the mixture was heated on a water-bath, under reflux, for 3 minutes and then slightly concentrated. The *hydroperbromide* crystallised in yellow plates which were collected on porous earthenware, dried in a vacuum, and reduced in sulphurous acid suspension with sulphur dioxide in the usual way (Hunter, *J. Chem. Soc.*, 1925, 127, 2023). On basification with ammonia (*d* 0·880) and recrystallisation from alcohol, 4'-fluoro-1-anilinobenzthiazole was obtained in glistening needles, m.p. 200-201°. (Found: S, 12·9. $C_{13}H_9N_2FS$ requires S, 13·1 per cent.). (ii) *Synthesis from 1-chlorobenzthiazole and p*-fluoroaniline.—A mixture of approximately equimolecular proportions of 1-chlorobenzthiazole and *p*-fluoroaniline was heated in a test tube over a large luminous flame until a violent reaction took place (compare Dyson, Hunter, and Soyka, *loc. cit.*). The product was basified with ammonia (*d* 0·880) and recrystallised from alcohol when 4'-fluoro-1-anilinobenzthiazole was obtained which had m. p. 200-201° alone, and when mixed with the specimen obtained from *p*-fluorodiphenylthiocarbamide.

p-Iodo-*s*-diphenylthiocarbamide, prepared as in the case of the fluorine analogue, separated from alcohol in crystals, m.p. 168°. (Found: S, 9·4. $C_{13}H_{11}N_2IS$ requires S, 9·0 per cent.).

4'-Iodo-1-anilinobenzthiazole (IX, R=I). (i) *The action of bromine on p*-iodo-*s*-diphenylthiocarbamide.—A suspension of the iododiphenylthiocarbamide (0·5 g.) in chloroform (5 c. c.) was treated with bromine (1 c. c.) and the mixture was heated under reflux on a steam-bath for 10 minutes. The *iodoanilinobenzthiazole* obtained by reduction of the *hydroperbromide* with sulphurous acid and basification with

ammonia, separated from alcohol-ethyl acetate in long prisms, m. p. 213° . (Found: S, 9.4. $C_{13}H_9N_2S$ requires S, 9.1 per cent.).

(ii) *Synthesis from 1-chlorobenzthiazole and p-iodoaniline*.—The black gum obtained by basifying the condensation product of 1-chlorobenzthiazole and *p*-iodoaniline, was dissolved in alcohol and the solution was kept. Slightly impure 4'-iodo-1-anilinobenzthiazole separated after some time in the form of grey coloured prisms, which was identified by m. p. and mixed m. p. with the specimen already described.

p-Cyanoaniline was conveniently prepared as follows: 28 G. of finely powdered *p* nitroaniline were made into a paste with 80 c.c. of 20 p.c. hydrochloric acid, and the mixture was diluted to 250 c. c. with water and cooled to 0° . This was diazotised with 28 c.c. of 50 p. c. sodium nitrite in the usual way, and the solution of the diazonium salt was rapidly added to cuprous cyanide solution (prepared from 200 c. c. of 25 p. c. copper sulphate solution and 200 c. c. of 25 p. c. potassium cyanide solution at 80° at 100° , and the mixture was kept at this temperature for 30 minutes. The *p*-cyanonitrobenzene obtained in this way was isolated by distillation in steam, superheated to 140° , in an efficient draught cupboard; m. p. 147° , yield 40 p. c. The nitro derivative (20 g.) mixed with granulated tin (40 g.) and 25 p. c. hydrochloric acid (60 c. c.) was gently heated on a steam-bath to start the reduction. The cyanoaniline obtained in this way was liberated by 30 p. c. sodium hydroxide in the form of a fine white suspension which was repeatedly extracted with ether, and the base thereafter crystallised from dilute alcohol, m. p. 86° , yield 50 p. c. *p*-Cyano-*s*-diphenylthiocarbamide, prepared by condensation of *p*-cyanoaniline and phenylthiocarbimide in alcoholic solution, separated from alcohol in silvery plates, m. p. $161-62^{\circ}$. (Found: S, 12.7. $C_{14}H_{11}N_3S$ requires S, 12.7 per cent.).

4'-Cyano-1-anilinobenzthiazole (IX, $R=CN$). (i) *Bromination of p-cyano-s-diphenylthiocarbamide*.—A suspension of the cyanodiphenylthiocarbamide (0.8 g.) in chloroform (8 c. c.) was gradually treated with bromine (1 c. c. in 1 c. c. of chloroform) when the thiocarbamide dissolved and a red gum separated. The mixture was heated on a water-bath, under reflux, for 3 minutes when hydrogen bromide was evolved. On slight concentration and cooling, the *hydroperbromide* crystallised in orange-red crystals which were dried in a vacuum and then reduced in sulphurous acid suspension with sul-

phur dioxide. On basification and recrystallisation from alcohol, 4'-cyano-1-anilinobenzthiazole was obtained in the form of aggregates of small needles, m. p. 206°. (Found: S, 12.7. $C_{14}H_9N_3S$ requires S, 12.75 per cent.).

(ii) *Synthesis from 1-chlorobenzthiazole and p-cyanoaniline.*—The base obtained by basification of the condensation product of the chlorobenzthiazole and p-cyanoaniline had m. p. 208° after recrystallisation from alcohol, and melted at 207° when mixed with the specimen of 4'-cyano-1-anilinobenzthiazole obtained from the bromination of the cyanodiphenylthiocarbamide.

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Preparation and Properties of Highly Concentrated Sols. Part II. Sols of Vanadium Pentoxide, Silicic Acid and Molybdic Acid.

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In a recent communication (Mittra and Dhar, *J. Indian Chem. Soc.*, 1932, **9**, 315) the methods of preparation and properties of highly concentrated sols of ferric, chromic and aluminium hydroxides have been investigated. In this communication, we are presenting the results obtained with concentrated sols of vanadium pentoxide, silicic acid and molybdic acid.

In several publications from these laboratories, (compare Ghosh and Dhar, *J. Phys. Chem.*, 1929, **33**, 1905) we have emphasised that, some properties of the sols of vanadium pentoxide, silicic, titanitic, antimonitic, tungstic and molybdic acids are fundamentally different from those of the sols of ferric, chromic, aluminium and other hydroxides, because the first group of sols is always associated with some amount of the acids in the dissolved condition. The behaviour of this group of hydroxide sols is far more complicated than that of the other hydroxide sols, *e. g.*, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, etc.

Vanadium Pentoxide Sol.

This sol was prepared according to the method of Biltz. A known weight of ammonium vanadate was made into a pasty mass in a pestle and mortar by adding small quantities of water and an equivalent amount of hydrochloric acid was added to it, drop by drop. The red precipitate obtained was removed to a filter paper and washed till it had the tendency to pass into colloidal condition. The precipitate was removed in a Jena glass bottle and vigorously shaken with the addition of a small quantity of water till a clear deep red sol was obtained. The sol was further purified by dialysis. The experiments were carried in a thermostat at 30°

From day to day as the dialysis was in progress, the concentration, density, viscosity and the coagulation of the sol by electrolytes were

determined with increasing purity of the sol. The following are the experimental results :

TABLE I.

Sol A. Conc. = 14.72 g. V_2O_5
per litre.

TABLE II.

Sol B. Conc. = 23.84 g. V_2O_5
per litre.

Viscosity of water at $30^\circ = 0.00803$.

Days dialysed.	Conc. g./litre.	Density.	Viscosity.	Days dialysed.	Conc. g./litre.	Density.	Viscosity.
0	14.72	1.010	0.02035	1	23.84	1.005	0.02984
1	14.20	1.009	0.02103	2	22.96	1.006	0.03068
2	13.48	1.011	0.02111	3	21.60	1.006	0.03229
3	13.36	1.009	0.02127	4	21.50	1.114	0.03281
6	13.12	1.009	0.23989	5	21.42	1.114	0.04489
7	13.00	1.012	0.36294	6	21.26	1.101	0.10355
8	12.44	1.013	Highly viscous	7	20.56	1.101	0.16870
				9	19.94	1.101	Highly viscous
				10	19.40	1.101	Jelly formed

The influence of the concentration on the viscosity of vanadium pentoxide sol of different degrees of purity was investigated and the results are as follows :

TABLE III.

Sol dialysed for 1 day.		Sol dialysed for 6 days.	
Conc. g./litre.	Viscosity.	Conc. g./litre.	Viscosity.
14.2	0.02103	13.12	0.23989
7.1	0.01282	6.56	0.01218
5.55	0.01026	3.28	0.01002
2.84	0.00959	2.624	0.00945
1.42	0.00851	1.312	0.00879
0.71	0.00834	0.656	0.00854

The coagulation of the vanadium pentoxide sol by potassium and barium chlorides was determined at 30° and 60° in order to find out the influence of temperature on coagulation of the sol. The following are the experimental results :

TABLE IV.

Sol A. Conc. = 14.72g. V_2O_5 per litre.

Total volume = 6 c.c.

Time = 1 hour.

Days dialysed.	Temp. 30°			Temp. 60°		
	Amt. of N/20-KCl.	Amt. of N/50-BaCl ₂ .	Ratio of ppt. conc.	Amt. of N/20-KCl.	Amt. of N/50-BaCl ₂ .	Ratio of ppt. conc.
0	1.81 c.c.	0.62 c.c.	7.30	2.00 c.c.	0.61 c.c.	8.2
1	1.75	0.61	7.17	1.95	0.60	8.125
2	1.59	0.57	7.00	1.78	0.56	7.95
3	1.48	0.54	6.85	1.66	0.53	7.83
6	1.38	0.52	6.63	1.54	0.50	7.70
7	1.26	0.50	6.30	1.43	0.49	7.31
8	1.18	0.49	6.02	1.35	0.48	7.00

Sol B. Conc. = 23.34 g. V_2O_5 per litre.

1	1.97	0.60	8.21	2.60	0.70	9.29
2	1.82	0.57	8.10	2.40	0.67	8.95
3	1.66	0.54	8.68	2.23	0.65	8.60
4	1.44	0.50	7.20	1.97	0.60	8.21
5	1.25	0.46	6.80	1.72	0.54	7.96
6	1.14	0.44	6.48	1.53	0.50	7.65
7	1.06	0.42	6.31	1.40	0.47	7.45
9	1.01	0.41	6.16	1.33	0.45	7.39
10	0.96	0.40	6.00	1.20	0.44	6.82

The influence of the concentration of a sol on the amounts of electrolytes necessary for coagulation was also investigated with vanadium pentoxide sol and the results are as follows:

TABLE V.

Conc. = 14.72 g. V_2O_5 per litre.

Total volume = 6 c.c.

Time = 1 hour.

Temperature = 30°.

Days dialysed.	Dilution.	Amt. of N/20-KCl.	Amt. of N/50-BaCl ₂ .	Ratio.
9	original	1.01 c.c.	0.41 c.c.	6.16
10	„	0.96	0.40	6.00
9	10 times	1.50	0.12	31.26
10	„	1.40	0.12	29.17

TABLE VI.

Sol B. Conc. = 23.34 g. V_2O_5 per litre.

Volume = 6 c.c. Time = 1 hour. Temp. = 30°.

Dilution.	Amt. of N/20-KCl to coagulate the fresh sol.	Amt. of N/20-KCl to coagulate the sol aged for 8 days.
B	1.12 c.c.	0.57 c.c.
B/5	1.37	0.47
B/10	1.49	0.42
B/20	1.56	0.38
B/40	1.58	0.36

Silicic Acid Sol.

A sol of silicic acid was prepared by the hydrolysis of silicon tetrachloride. A Kahlbaum sample of silicon tetrachloride was added drop by drop to ice cold water, and the sol thus formed was purified by dialysis.

The density, viscosity and coagulation of the sol were also investigated from day to day as the dialysis progressed. The results are as follows :

TABLE VII.

Days dialysed.	Sol A.			Sol B.		
	Conc.	Density at 30°.	Viscosity at 30°.	Conc.	Density at 30°.	Viscosity at 30°.
0	25.78	1.200	0.00965	32.32	1.223	0.00823
1	22.78	1.116	0.00983	30.48	1.182	0.00834
2	21.96	1.112	0.00994	29.12	1.143	0.00845
3	21.34	1.009	0.01047	29.00	1.110	0.00964
4	21.04	1.012	0.01256	28.23	1.098	0.00998
5	20.76	1.014	0.01269	27.62	1.100	0.01142
6	20.72	1.010	0.01312	27.02	1.09	0.01226
7	20.68	1.012	0.01508	26.34	1.07	0.02284
8	20.58	1.010	0.02084	25.88	1.06	0.1496
9	20.40	1.010	0.14460	25.34	1.06	0.2342
10	—	—	Highly viscous	—	—	Highly viscous

The influence of concentration on the viscosity of silicic acid sol of different degrees of purity was investigated and the results are as follows :

TABLE VIII.

1st day of dialysis.		8th day of dialysis.	
Conc.	Viscosity.	Conc.	Viscosity
24.62	0.01445	19.55	0.14980
12.31	0.01123	9.78	0.01504
6.15	0.00984	4.89	0.01266
4.92	0.00942	3.91	0.01082
2.46	0.00856	1.95	0.00981
1.23	0.00839	0.98	0.00877

Freshly prepared silicic acid sol cannot be coagulated by uni- and bivalent electrolytes but it becomes unstable in the presence of a small quantity of alkali. Hence the sol was always coagulated in the presence of small quantities of ammonium hydroxide and the results are as follows :

TABLE IX.

Conc. = 32.32 g. SiO_2 per litre. 0.2 C.c. of $\text{N-NH}_4\text{OH}$ added.

Time = 1 hour. Total volume = 6 c.c.

Days dialysed.	Temp. 30°			Temp. 60°		
	Amt. of 2N-KCl.	Amt. of N/10-BaCl ₂ .	Ratio.	Amt. of 2N-KCl.	Amt. of N/10-BaCl ₂ .	Ratio.
0	1.86 c.c.	0.80 c.c.	46.5	1.20 c.c.	0.66 c.c.	36.36
1	1.80	0.76	47.37	1.17	0.63	37.14
2	1.72	0.70	49.14	1.06	0.55	38.54
3	1.65	0.65	50.50	1.02	0.52	39.23
4	1.58	0.60	52.66	0.98	0.46	42.60
5	1.50	0.55	54.54	0.96	0.43	44.65
6	1.48	0.52	56.92	0.90	0.39	46.15
7	1.44	0.50	57.60	0.86	0.36	47.77
8	1.41	0.47	60.00	0.84	0.33	50.90
9	1.40	0.45	62.20	0.83	0.32	51.87

In order to study the influence on silicic acid sol, coagulation experiments were carried on with the sol sensitised by different amounts of ammonium hydroxide and the results are recorded below :

TABLE X.

Total volume = 6 c.c. Time = 1 hour. Temp. = 30°.

Sol dialysed for 2 days.		Conc = 7.52 g. SiO ₂ per litre.	
Amount of 1.3 N-NH ₄ OH added.	Amt. of 3N-KCl necessary for coagulation.	Amt. of N/10- BaCl ₂ , necessary for coagulation.	Ratio of ppt. conc., mono/bi.
0.20 c.c.	0.96 c.c.	1.01 c.c.	28.5
0.25	0.95	0.51	55.9
0.30	0.94	0.41	68.8
0.40	0.92	0.31	89.0

TABLE XI.

Sol dialysed for 4 days. Conc. = 5.78 g. SiO₂ per litre.

Total volume = 6 c.c. Time. = 1 hour. Temp. = 30°.

Amt. of N-NH ₄ OH added.	Amt. of 3N-KCl necessary for coagulation.	Amt of N/10-BaC necessary for coagulation.	Ratio of ppt. c mono/bi.
0.2 c.c.	0.90 c.c.	0.23 c.c.	117.4
0.25	0.88	0.21	125.7
0.30	0.86	0.20	129.0
0.40	0.85	0.19	134.2

Molybdic Acid Sol.

Molybdic acid sol was prepared by the action of nitric acid on a concentrated solution of ammonium molybdate. The amount of nitric acid added was such that the white precipitate formed just redissolved. The sol was purified by dialysis.

The viscosity of the sol was practically the same as that of water at the same temperature, although the sol was highly concentrated.

The sol was coagulated by potassium chloride and barium chloride and the results are as follows :

TABLE XII.

Conc. = 128.62 g. MoO_3 per litre.

Vol. of the sol = 2 c.c. Total vol. = 6 c.c. Time = 1 hour.

Days dialysed.	Temp. 30°			Temp. 60°		
	Conc. necessary to coagulate		Ratio.	Conc. necessary to coagulate		Ratio
	KCl.	BaCl ₂ .		KCl.	BaCl ₂ .	
1	0.1 N	0.00533 N	18.74	0.08 N	0.0035 N	22.86
2	0.0129 N	0.00133 N	9.70	0.0065 N	0.00066 N	9.85
3	0.00133 N	0.000166 N	8.00	0.0033 N	0.0004 N	8.25
4	0.000766 N	0.000107 N	7.16	0.0025 N	0.00032 N	7.81
5	0.00055 N	0.000093 N	5.91	0.00216 N	0.00031 N	7.00
6	0.00033 N	0.000070 N	4.71	0.00183 N	0.000296 N	6.18
7	0.00023 N	0.000053 N	4.34	0.00133 N	0.000276 N	4.84
8	0.000166 N	0.000043 N	3.86	0.001033 N	0.000266 N	3.88

Discussion.

From the foregoing tables, it will be clear that the viscosity of vanadium pentoxide and silicic acid sols increases markedly with their purity. This behaviour appears to be more pronounced with silicic acid sol than with vanadium pentoxide sol. The viscosity of undialysed and freshly prepared sol B of silicic acid, which is quite concentrated, does not differ very much from that of water; but after dialysis lasting for a week, the viscosity is greatly increased.

In order to obtain strictly comparable results we must take into consideration the influence of ageing on the properties of these sols. It has been emphasised in several publications that colloids have no definite composition, but it changes with time. The viscosity of sols of silicic and vanadic acids increases on ageing as

will be evident from the following results (cf. Ghosh and Dhar, *loc. cit.*).

Vanadium pentoxide sol. Conc. = 1.098 g./litre.		Silicic acid sol. Conc. = 12.075 g./litre.	
Date.	Viscosity (compared with water.)	Date.	Viscosity at 30°
4 Dec. 1922	1.080	7 April 1927	0.00872
6 Dec. 1922	1.085	2 May 1927	0.00919
8 Dec. 1922	1.100	13 July 1927	0.01121
18 Dec. 1922	1.110		
28 Dec. 1922	1.192		

Recently Chakravarti (D.Sc. Thesis, Allahabad University) has obtained exactly similar results on ageing with more concentrated sols of vanadium pentoxide.

On comparing these results on the influence of ageing on viscosity of sols of vanadium pentoxide and silicic acid with those obtained regarding the influence of purity on the viscosity of these sols, it will be clear that the latter influence is much more prominent than the former one. Thus with vanadium pentoxide sol, the ageing effect in 14 days is only a three per cent. increase of viscosity, whilst on purifying the sol for a week or so by dialysis, the viscosity of sols A and B are enormously increased, although the concentrations of the sols are less than those of the freshly prepared undialysed ones. Similarly with silicic acid sol, the viscosity increases about six per cent. in 25 days due to ageing, whilst after ten days dialysis, both the sols A and B become highly viscous. Consequently, even when we take into account the increase of viscosity of these sols on ageing, it will be evident that the viscosity increases with the dialysis of the sols. As the sols become purer and purer on dialysis, the adsorbed electrolyte becomes less and the electric charge on the particles of the sol decreases. Along with the decrease of the charge, the viscosity of the sol markedly increases. Hence these results obtained with vanadium pentoxide and silicic acid sols are in agreement with the conclusion of Dhar that the greater the purity and less the charge on the sol, the greater is its viscosity.

Chakravarti, Ghosh and Dhar (*J. Phys. Chem.*, 1930, **34**, 830) have deduced that if $N_1, N_2, N_3, \dots, N_x$ be the precipitating concentrations of uni-, bi-, tri-, ..., x valent ions, then

$$N_1 : N_2 : N_3 : \dots : N_x = 1 : \frac{1}{2}a : \frac{1}{3}a : \dots : \frac{1}{x}a^{x-1} \quad \text{where} \quad a = e^{-\frac{qe}{Dr}} \frac{Dr}{KT}$$

that is a lies between 0 and 1 and is a proper fraction, q = charge on

the colloid, D =dielectric constant of the medium, r =distance of the double layer, T =absolute temperature and K =Boltzmann constant. It follows from the foregoing relation that when T or D increases or q decreases, α tends to become unity. In other words, as the charge on the colloid particles decreases, the precipitating concentration of uni-, bi-, and trivalent ions tend to be in the ratio $1:\frac{1}{2}:\frac{1}{3}$.

Moreover, it follows from the above relation that when the temperature is increased, there should be a tendency of the precipitating concentrations to arrange in the ratio $1:\frac{1}{2}:\frac{1}{3}$.

The experimental results obtained with vanadium pentoxide and molybdic acid sols show that the ratio of the precipitating concentrations with potassium chloride and barium chloride appreciably decreases with the purity of the sols and these results are in agreement with the theoretical deductions of Chakravarti, Ghosh and Dhar already referred to.

It has already been stated that sols of vanadium pentoxide, silicic acid, molybdic acid and tungstic acid are always associated with the respective substance in the dissolved condition. With time the dissolved molecules, existing in large amounts in freshly prepared sols, agglomerate and form colloid particles, but on increasing the temperature of freshly prepared sols of vanadic and molybdic acids, the amount of dissolved substance is increased as will be evident in the case of vanadic acid from the following results obtained by Ghosh and Dhar (*loc. cit.*) with vanadium pentoxide sol:

Concentration of sol = 7.41 g. V_2O_5 per litre.

Sol.	Amounts of V_2O_5 dissolved in 10 c.c. of sol.
Unboiled sol on 10 Nov. 1927	0.0038 g.
Unboiled sol on 12 Dec. 1927	0.0033
Boiled sol	0.0072

Now the stability of the sols of vanadic and molybdic acids increases with the increase in the amount of the dissolved acids, which yield negative ions adsorbable by the sols, and these sols are negatively charged. It is evident from the results recorded in this paper that the amounts of univalent positive ions required to coagulate these sols are much greater than the amounts of bivalent positive ions and consequently slight change in the stability of the sols is likely to

affect the precipitating concentration of potassium chloride more than that of barium chloride. Thus the ratio of the precipitating concentrations of potassium and barium chlorides is greater when the coagulation is carried at 60° than at 30° , because of the increased stability of the sol at 60° . This behaviour is observed only with the freshly prepared sols of vanadium pentoxide. With the aged sol of vanadium pentoxide, the amount of potassium chloride required for coagulation is less at 60° than at 30° (*cf.* Dhar and Satya Prakash, *J. Phys. Chem.*, 1930, **34**, 954).

The results on the coagulation of silicic acid sol by potassium and barium chlorides at 30° and 60° show that at 60° , the sol becomes unstable for both the electrolytes and the ratio of the precipitating concentration of potassium chloride to that of barium chloride is much less at 60° than at 30° . Consequently, this sol shows a different behaviour regarding its stability at higher temperatures from that of vanadic and molybdic acid sols. In precipitating silicic acid sol by electrolytes we have observed that the sol was extremely stable towards electrolytes and in order to effect precipitation by potassium and barium chlorides, the sol was mixed with traces of ammonium hydroxide, which sensitises the sol. In a previous communication, Ghosh and Dhar (*loc. cit.*) showed that the sensitising influence of traces of alkali is due to the formation of soluble silicates and dissolution of some of the complex and aggregated molecules of silicic acid.

It is obvious that the dissolution and the formation of silicate by the addition of traces of ammonium hydroxide is more pronounced at higher temperatures than at lower ones, and consequently, the sensitising influence of ammonium hydroxide towards silicic acid is greater at 60° than at 30° and the sol is less stable at 60° than at 30° .

Moreover, it will be seen that in the coagulation of silicic acid sol, which has been rendered unstable towards electrolytes by the addition of small quantities of ammonium hydroxide, the amount of barium chloride required for coagulation decreases more rapidly than the quantities of potassium chloride necessary for coagulation as the purity of the sol increases. It has also been observed in Tables X and XI that the decrease in the amount of barium chloride necessary for coagulating silicic acid sol in presence of increasing amounts of ammonium hydroxide acting as a sensitiser, is more pronounced than the decrease of the amount of potassium chloride under identical conditions.

It appears, therefore, that the sensitising influence of ammonium hydroxide on silicic acid sol is more pronounced on its coagulation by bivalent electrolytes than by monovalent ones and the increased purity of the silicic acid sol affects more markedly its coagulation by barium chloride than by potassium chloride. Hence these two properties of silicic acid sol appear to be related and seem to be due to the existence of the sol particles of different degrees of agglomeration along with the dissolved silicic acid and the possibility of forming sparingly soluble barium silicate on the addition of barium chloride to silicic acid containing small amounts of ammonium hydroxide. •

• These sols become unstable towards their coagulation by electrolytes on ageing as is generally observed with other sols. This behaviour may be ascribed to the formation of bigger aggregates from the colloidal particles on ageing and the consequent decrease in the number of the adsorbed stabilising ions. Moreover, these sols also become unstable on being heated specially when the sols are aged. We are of opinion that heating accentuates the ageing phenomenon specially with silicic acid sols and the stabilising ions are given out and thus the sols become unstable towards their coagulation, silicic acid sol being very sensitive to heat specially when aged. Thus a sol of silicic acid containing 22.54 g. of SiO_2 per litre sets to a stiff jelly on heating. Similar heat sensitivity of silicic acid sols has been reported by Flemming (*Z. Phys. Chem.*, 1902, **41**, 427) and Pauli and Valko (*Kolloid Z.*, 1926, **38**, 289). In this respect silicic acid behaves like some typical lyophillic colloids. In previous papers (Dhar and Gore, *J. Indian Chem. Soc.*, 1929, **6**, 31, 641) it has been reported that when the sols of ferric, chromic, aluminium and other hydroxides become highly pure they behave like lyophillic colloids regarding their viscosity. From the results recorded in Tables III and VIII, it appears that with pure sols of vanadium pentoxide and silicic acid, the viscosity-concentration relation is allied to that of a typical lyophillic colloid. The viscosity increases enormously in the concentrated condition and the viscosity-concentration curves are very steep.

The experimental results in Tables V and VI show that when vanadium pentoxide sol is freshly prepared, it requires greater amounts of potassium chloride for coagulation in the diluted condition than in the concentrated one. On the other hand, the aged sol requires smaller quantities of electrolytes for coagulation when diluted than the concentrated sol. The sols of vanadium pentoxide, silicic acid, molybdic acid, etc. always contain the respective acids in the dissolved

condition and the amount of acid present in the dissolved condition decreases with time due to their agglomeration to form sol particles. The negative ions given out by the acids are adsorbed by the sols and thus their electric charge is mainly due to this ionic adsorption. The antagonistic action of this stabilising ion is more pronounced in the coagulation of the diluted sol by an univalent ion than in the case of the concentrated sol, partly because of the greater ionisation of the dissolved acid when the sol is diluted. Hence larger quantities of potassium chloride are necessary for coagulating a freshly prepared and diluted sol than the concentrated one. When the sol becomes aged, the amount of dissolved acid existing along with the sol decreases and the influence of the stabilising ion becomes less marked and the sol requires smaller quantities of potassium chloride for coagulation when diluted than that required for coagulating the original sol. It appears that the behaviour of these sols is much more complicated than that of sols of ferric, chromic, and aluminium hydroxides. Further work with these sols, which are associated with the respective substances in the dissolved condition, is in progress.

Summary.

1. The viscosity of sols of vanadium pentoxide and silicic acid increases considerably with their purity. With the pure sols, the viscosity-concentration curves are very steep and resemble those of some lyophilic colloids. The viscosity of even a concentrated sol of molybdic acid is practically the same as that of water.

2. The ratio of the coagulating concentrations of potassium and barium chlorides decreases with the purity of sols of vanadium pentoxide and molybdic acid. Silicic acid sol can be coagulated by potassium and barium chlorides only when sensitised by ammonium hydroxide or any other alkali. In this case the ratio of the precipitating concentrations of potassium and barium chlorides increases with the purity of the sol.

3. The sensitising influence of ammonium hydroxide on silicic acid sol is more pronounced on its coagulation by bivalent ions than by monovalent ones. Moreover the increased purity of silicic acid sol affects more markedly its coagulation by bivalent ions than monovalent ions. These two properties appear to be related and are quite peculiar to silicic acid sol.

4. With silicic acid sol the ratio of the coagulating concentrations of potassium and barium chlorides is smaller at 60° than at 30°, whilst with vanadium pentoxide and molybdic acid the same ratio is greater at 60° than at 30°, specially when the sols are freshly prepared.

5. The properties of these sols are certainly more complicated than those of the other hydroxide sols, because these sols always contain the respective acids in the dissolved condition and these molecules have a tendency to agglomerate into sol particles.

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Preparation and Properties of Highly Concentrated Sols. Part III. Sols of Zirconium Hydroxide.

By R. D. SHARMA AND N. R. DHAR.

In recent communications, we have investigated the preparation and properties of highly concentrated sols of some metallic hydroxides. In this paper, we are submitting the results obtained with zirconium hydroxide sol. At first we tried to prepare a concentrated sol of zirconium hydroxide by peptising a freshly prepared precipitate of zirconium hydroxide by a solution of zirconium nitrate. A concentrated solution of zirconium nitrate was prepared and drop by drop, ammonium hydroxide was added to it till the precipitate first formed redissolved on shaking. The sol thus formed was concentrated by boiling. In this way a sol containing 166.0 g. of ZrO_2 per litre could be prepared. This sol looked like glycerol and was highly viscous but contained a considerable amount of nitrate ion. As the sol prepared by the peptisation method is impure, we prepared our sols by the hydrolysis of zirconium nitrate solution and subjected it to dialysis. After dialysis lasting for one week at the ordinary temperature, the sol thus obtained was concentrated by boiling. By this method, a sol containing 402 g. ZrO_2 per litre was obtained. The purity of the sol, i. e., ZrO_2/NO_3 was 2.5. In order to obtain a purer sol, this concentrated sol was diluted and subjected to hot dialysis and a sol containing 100.2 g. ZrO_2 per litre with a purity of 6.6 was obtained (sol A). The sol was clear in transmitted light but opalescent in reflected light and was slightly yellowish. On attempting to concentrate the sol further it becomes a jelly. It is evident, therefore, that if a sol of greater purity is to be prepared, its concentration cannot be as high as that of the sol A. Hence a portion of the sol A was diluted and subjected to dialysis. In this way, a sol containing 55.2 g. ZrO_2 per litre with a purity of 16.2 was obtained (sol B). This sol was colourless and was perfectly clear in both transmitted and reflected light. It was highly viscous and looked like glycerol. Any further attempt to get this sol in

a purer state by cold or hot dialysis leads to its gelation or the formation of a glassy mass.

The concentration of the sol was determined by evaporating in a platinum crucible a known volume of the sol to dryness and igniting it and weighing it as ZrO_2 . The amount of nitrate was estimated by treating it with Devarda's alloy and distilling off the ammonia and absorbing it by a standard solution of sulphuric acid.

Coagulation of the Sols by Electrolytes.

The sols being highly viscous and concentrated, the coagulation experiments have been carried on after diluting the sol 10 times with conductivity water. The sols are positively charged but could not be readily coagulated by even a saturated solution of potassium chloride. Hence the coagulation experiments were carried on with potassium bromate and potassium sulphate and the results are as follows:

TABLE I.

Coagulation time = 1 hour.

	Coagulating concentration of		Ratio.
	$\text{KBrO}_3(a)$.	$\text{K}_2\text{SO}_4(b)$.	a/b
Sol A	0.1666 N	0.00516 N	32.2

TABLE II.

Coagulation time = 1 hour.

	Coagulating concentration of		Ratio.
	$\text{KBrO}_3(a)$.	$\text{K}_2\text{SO}_4(b)$.	a/b
Sol B	0.06613 N	0.001666 N	39.6

The sols were stabilised by adding a solution of zirconium nitrate containing 1.0436 g. of the salt in 100 c. c. of the solution. 2 C. c. of this solution were added to 10 c. c. of the original sol. 10 C. c. of this mixture were diluted to 100 c. c. and this was used for the coagulation experiments and the results are recorded below.

TABLE III.

Coagulation time=1 hour.

	Coagulating concentration of		Ratio.
	KBrO ₃ (a).	K ₂ SO ₄ (b).	a/b
Sol A	0.1895 N	0.005249N	36.1
Sol B	0.08287N	0.00175N	47.8

Hence it appears that as the sol becomes impure and consequently more stable by the adsorption of Zr. ions, the ratio of the coagulating concentrations of mono- and bivalent electrolytes increases and this is in agreement with the results obtained with other hydroxide sols and follow the theoretical deduction of Chakravarti, Ghosh and Dhar (*J. Phys. Chem.*, 1930, **34**, 330).

The influence of concentration of the sol on its coagulation has also been studied and the results are as follows:

TABLE IV.

Coagulating time=1 hour.

	Coagulating concentration of		Ratio.
	KBrO ₃ (a).	K ₂ SO ₄ (b).	a/b
Sol A	0.1728N	0.005416N	31.6
Sol B	0.06707N	0.001875N	35.5

It will be observed that with this sol the relations that the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion, is applicable.

One interesting fact is that the coagulum in the case of the sol A which is less pure and less viscous than sol B appears white, whilst the coagulum obtained from the sol B which is purer and more viscous appears almost transparent and less white than that obtained in the case of sol A. Similar results are obtained with stannic hydroxide sols of different degrees of purity. It appears that the coagulated mass obtained from a highly hydrated and viscous sol is also associated with large quantities of water and appear transparent.

Viscosity of the Sols.

The viscosities of both the sols A and B at different concentrations were determined at 22° by Ostwald's viscosimeter and the results are recorded below :

TABLE V.

Viscosity of water at 22° = 0.009606.

Sol taken = 5 c.c.

Conc. of sol.	Sol A.		Sol B.	
	Density.	Viscosity.	Density.	Viscosity.
a (original)	1.104	0.23301	1.0568	1.71575
a/2	1.050	0.03326	1.026	0.20691
a/4	1.024	0.01806	1.012	0.04148
a/8	1.013	0.01192	1.0058	0.01973
a/16	1.0052	0.01072	1.0023	0.01344

The viscosity of these sols after the addition of 2 c.c. of zirconium nitrate solution containing 1.0436 g. of the salt in 100 c.c., to 10 c.c. of the original sols has also been determined and the results are compared with those obtained after adding 2 c.c. of water to 10 c.c. of the sols,

TABLE VI.

Conc. of sol.	Sol A.		
	Viscosity of pure sol.	Viscosity of sol mixed with $\text{Zr}(\text{NO}_3)_4$.	Viscosity of sol mixed with water.
a	0.23301	0.07566	0.08260
a/2	0.03326	0.02399	0.02590
a/4	0.01806	0.01738	0.01753
a/8	0.01192
a/16	0.01071
	Sol B.		
	Viscosity of pure sol.	Viscosity of sol mixed with $\text{Zr}(\text{NO}_3)_4$.	Viscosity of sol mixed with water.
a	1.71575	0.99507	1.68259
a/2	0.20691	0.13784	0.18099
a/4	0.04148	0.02848	0.03869
a/8	0.01973
a/16	0.01344

Just as in the case of concentrated sols of ferric, chromic, and aluminium hydroxides, the viscosity of the highly concentrated zirconium hydroxide sol appreciably diminishes to a limiting value on repeating the viscosity measurements.

The surface tension of the sol was determined by the capillary rise method. We also attempted to measure the surface tension of the highly viscous sols by Du Nouy's method but no concordant results were obtained. The results obtained by the capillary rise method are recorded in Table VII. The specific conductivity of the sols was also determined and the results recorded in Table VIII.

TABLE VII.

TABLE VIII.

Temperature = 22°.		Sol.	Sp. cond. $\times 10^{-3}$.
Sol.	Surface tension.		
Sol A	70.2	Sol A	1.196
Sol A + $\text{Zr}(\text{NO}_3)_4$ solution	70.61	Sol A aged for 10 days	1.286
Sol A/10	71.32	Sol A/10	0.274
Sol B	71.66	Sol A/10 aged for 10 days	0.285
Sol B + $\text{Zr}(\text{NO}_3)_4$ solution	71.14	Sol B	0.425
Sol B/10	71.87	Sol B aged for 10 days	0.452
Water	72.22	Sol B/10	0.0698
		Sol B/10 aged for 10 days	0.0949

It appears from the foregoing results on the measurements of the specific conductivity (Table VIII) that with time the specific conductivity increases probably because of the giving out of the adsorbed electrolyte by the colloid particles on ageing.

It has already been reported in a previous communication that when a highly concentrated sol of chromium hydroxide is allowed to dry up in the dark, a transparent residue is left which when mixed up with water passes back to a sol condition. Similar reversible behaviour is observed with zirconium hydroxide sol. When these concentrated sols of zirconium hydroxide are allowed to dry up in a desiccator over sulphuric acid in the dark, a transparent residue is left which swells up on the addition of water and passes into the sol state. When however, the sols are dried in the sun or on a water-bath, a part of the reversibility is lost. It, appears, therefore, that when the drying of the sol is rapid, the colloid particles get dehydrat-

ed and the reversibility disappears but when the sol is allowed to dry slowly in the dark, the dried mass is completely reversible and in this respect, zirconium hydroxide behaves like a lyophilic colloid.

The highly concentrated sols of zirconium hydroxide prepared by us are highly viscous. Sol B, which contains practically half the amount of zirconium hydroxide as present in sol A, is about 8 times more viscous than sol A. This is due to the fact that sol B is more pure (purity 16.2) than sol A (purity 6.6). Moreover, the viscosity of these sols is appreciably decreased on the addition of the peptising electrolyte, zirconium nitrate, which increases the charge on the colloid particles. Hence, these results conclusively prove that greater the purity of the sol and less the charge on the colloid particles, the greater is its viscosity.

From Table VI, it will be clear that the viscosity-concentration curve of a highly concentrated sol of zirconium hydroxide is steep and that this is more steep with the purer sol B than with A. Consequently, from the point of view of viscosity, the concentrated sols of zirconium hydroxide, like other hydroxide sols investigated in this laboratory behave as a typical lyophilic colloid. Moreover, the surface tension of zirconium hydroxide sol is appreciably less than that of water.

Summary.

1. By hydrolysing concentrated solutions of zirconium nitrate and by hot dialysis of the solution, highly concentrated sols of zirconium hydroxide containing 100.2 g. ZrO_2 i.e., 0.8172 g. mole ZrO_2 per litre with a purity 6.6 and 55.2 g. ZrO_2 i.e., 0.4502 g. mole ZrO_2 per litre with a purity of 16.2 have been obtained.

2. These concentrated sols are highly viscous and the greater the purity of the sol, the greater is its viscosity. The viscosity of these sols decreases when their electric charge is increased by the addition of zirconium nitrate solution. The viscosity-concentration curves of concentrated zirconium hydroxide sols are steep. The purer the sol the more steep the viscosity-concentration curve.

3. The ratio of the coagulating concentrations of potassium bromate and sulphate increases when zirconium nitrate is added to stabilise the sols.

4. The surface tension of concentrated sols of zirconium hydroxide is appreciably less than that of water.

5. The specific conductivity of the sols increases on ageing.

6. When these highly concentrated sols are allowed to dry slowly in the dark, the dry residue swells on adding water and passes into the sol again.

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Relation between Charge and Stability of Colloidal Solutions of Gold and Ferric Hydroxide Dialysed to Different Extents.

BY B. N. DESAI, G. M. NABAR AND P. M. BARVE.

It is believed by most colloid chemists that the stability of a colloid, as determined by the coagulating concentration of an electrolyte, depends on the charge on its particles and that the greater the charge the greater will be the stability. The results of coagulation of colloids by electrolytes as well as the effect of dialysis on the stability of colloids have been explained on the basis of this view. Mukherjee, Choudhury and Rai Choudhury (*J. Indian Chem. Soc.*, 1927, **4**, 493) working on colloidal arsenious sulphide found that the stability is not directly related to the charge as is generally believed to be; in some of the results they found a greater stability in spite of smaller charge on the colloid. Their conclusion is however based on the results obtained with mixtures of electrolytes as well as with single electrolytes containing organic anions. It was therefore considered necessary to investigate if the same behaviour is also shown by other sols under much more simple conditions.

It is well known, that although in most cases, the stability of the sol decreases with the progress of dialysis, colloidal gold prepared by the formaldehyde method becomes more stable towards electrolytes with progress of dialysis up to a certain stage, after which stability towards electrolytes decreases (Freundlich, "Colloid and Capillary Chemistry," 1926, English Translation, p. 506). It has also been shown by Galecki (*Z. anorg. Chem.*, 1912, **74**, 196 *et seq*) that the cataphoretic speed of gold sol increases with the progress of dialysis along with an increase in the flocculation value. In what follows results of simultaneous measurements of charge and flocculation value with potassium chloride of colloidal solutions of

gold and ferric hydroxide dialysed to different extents have been given.

EXPERIMENTAL.

Preparation of colloidal solutions.—Gold sol was prepared by Zsigmondy's nucleus method in batches of 100 c.c. Ferric hydroxide sol was prepared in instalments of 500 c.c. by adding 80 c.c. of a 45% solution of ferric chloride drop by drop to 500 c.c. of boiling distilled water ; the mixture was stirred all the time and the resulting brown red sol was boiled for $\frac{1}{2}$ hour.

The sols were transferred to parchment paper bags for dialysis. The bags were previously treated with distilled water to remove soluble matter. The outer water was changed twice a day. Suitable amounts of colloids were withdrawn every time for experiments by means of a pipette.

Method of measuring the charge.—The charge was measured according to Mukherjee's improved U-tube method (*Proc. Roy. Soc.*, 1923, **A**, 103, 102 ; also Mukherjee, Choudhury and Rai Choudhury, *loc. cit.*). The electrodes were put in the side bulbs and not in the limbs of the U-tube in order to avoid the disturbing effect of electrolysis on the sharpness of the boundary.

Mukherjee, Raichoudhury and Bhattacharyya (*J. Indian Chem. Soc.*, 1928, **5**, 735) have shown that unless the upper liquid has got the same ionic composition as the intermicellary liquid the results of charge measurements are sure to be erroneous. Mukherjee, Raichoudhury and Biswas (*J. Indian Chem. Soc.*, 1931, **8**, 373) have also shown that the use of ultrafiltrate as the upper liquid does not give reliable results. The upper liquid in our measurements of gold sol consisted of solution of potassium chloride having the same conductivity as the colloid ; it gave quite satisfactory results. In the case of ferric hydroxide the upper liquid was prepared in the same manner as given by S. N. Mukherjee (*Kolloid Z.*, 1930, **52**, 68).

We also performed some experiments in case of ferric hydroxide sol to see if the dialysate could be used as an upper liquid (*of. "Colloid and Capillary Chemistry"*, Eng. Trans., p. 372). It was found that in the initial stages in the case of sols dialysed for short periods and containing still appreciable amounts of HCl and FeCl₃, the dialysate obtained by keeping distilled water in contact with the colloid in the parchment bag for about 86 hours could be used as a satisfactory upper liquid. The results obtained by using the dialysate

FIG. 1

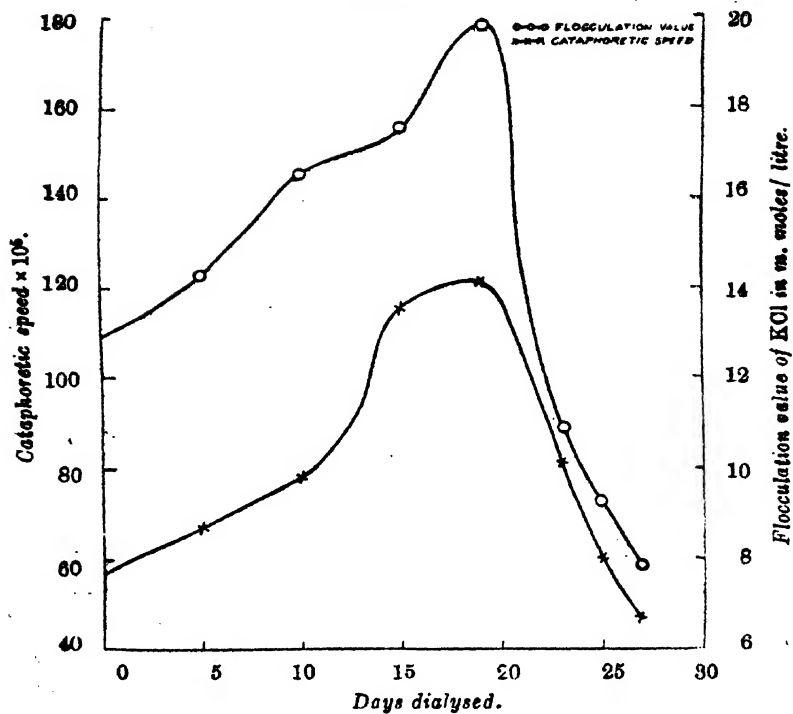
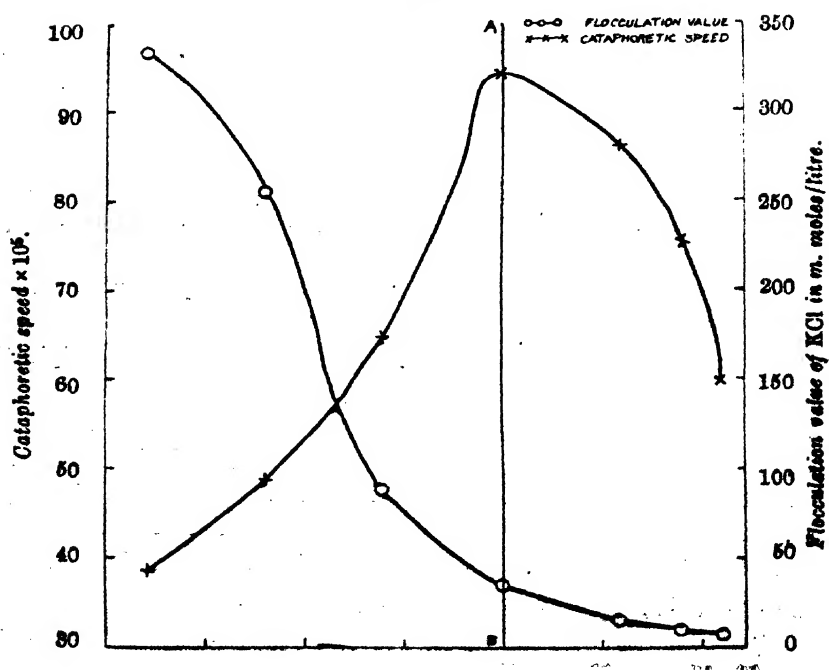


FIG. 2.



Discussion.

From Fig. 1 it is seen that in the case of gold sol both charge (assuming that the rate of migration represents the density of the charge) and flocculation value behave similarly on subjecting the colloid to dialysis; they first increase with the progress of dialysis, reach a maximum and then begin to decrease simultaneously. In the case of ferric hydroxide sol (Fig. 2) although with the progress of dialysis the charge first increases and then decreases, the flocculation value continuously decreases.

The initial increase in charge with the progress of dialysis might be due to the following effect.

We have observed that the cataphoretic speed of colloidal gold and of ferric hydroxide first increases and then decreases on addition of small increasing amounts of KOH and of HCl and FeCl₃, respectively (unpublished results). This is due to "preferential" adsorption of the similarly charged ions in the beginning, the word "preferential" indicating that the ions are adsorbed in the inner sheet of the double layer. The amounts of stabilising ions (OH ion in case of gold sol and H and Fe ions in case of ferric hydroxide sol) in the sol continuously decreases with the progress of dialysis. The process of dialysis can be taken as the reverse of the above process, the amounts of the stabilising agent initially present in the sol being appreciably more than what will correspond to the maximum in the cataphoretic speed-concentration curve of the colloid with the particular electrolyte and therefore with the progress of dialysis the charge on the colloid will first increase and then decrease (cf. Freundlich, *loc. cit.*). On extreme dialysis the colloid will coagulate due to the removal of the stabilising ions from the double layer. It is therefore likely that various colloidal solutions when subjected to dialysis might show a first increase and then a decrease or a continuous decrease in the cataphoretic speed according to whether the amount of stabilising agent is more or equal to or less than what will correspond to the maximum in the cataphoretic speed-concentration curve of the sols with particular electrolytes.

The continuous decrease in the flocculation value in the case of ferric hydroxide sol, instead of an increase first and decrease thereafter as in the case of the cataphoretic speed, can be due to either or both the following effects:

(1) Rona and Michaelis (*Biochem. Z.*, 1919, 97, 85) have found that the amount of H ion adsorbed by charcoal was greater in the presence of potassium chloride than without it and that it reached a maximum with increasing amounts of potassium chloride (*cf.* Parks and Bartlett, *J. Amer. Chem. Soc.*, 1927, 49, 1698). Mukherjee, Choudhury and Rai Choudhury (*loc. cit.*) have found that the charge on colloidal arsenious sulphide in the presence of small amounts of an electrolyte increased on the addition of another electrolyte having a common coagulating ion but a different similarly charged ion. On the addition of KCl the colloid can be said to be under the influence of a mixture of electrolytes ($\text{KCl} + \text{HCl} + \text{FeCl}_3$) and therefore if we presume that on its addition more H and Fe ions are adsorbed in the inner sheet of the double layer, the charge on the colloid will also increase and a larger amount of potassium chloride will be required to coagulate the sol. With the progress of dialysis, the concentration of intermicellary HCl and FeCl_3 decreases and the charge on the particles increases. If KCl is now added the increase in the adsorption of H and Fe ions may not be so much as to raise the final charge on the particles to the value which would obtain in the case of a sol dialysed for a shorter period. (Measurements of cataphoretic speed of colloidal solution of ferric hydroxide, dialysed to different extents, in the presence of varying amounts of HCl and KCl as well as $\text{HCl} + \text{KCl}$ indicate that the adsorption of H ions does increase under certain circumstances in the presence of KCl—unpublished results.) If this be the case a smaller amount of the electrolyte will be required to coagulate the dialysed sol in spite of the higher initial charge on its particles. This mechanism will go on till the maximum in the cataphoretic speed-dialysis curve is reached. After the maximum (the portion of the curve to the right of line AB in Fig. 2) as the charge on the colloid continuously decreases with further progress of dialysis progressively smaller amounts of KCl will be required to coagulate the sol.

In the case of the gold sol the stability and charge showed a similar behaviour even during the period when the charge increased because the amount of electrolytes initially present in the intermicellary liquid (KOH and KCl) being very small, addition of KCl to the colloid may not have increased the adsorption of either or both OH and Cl ions in the inner sheet of the double layer as in the case of ferric hydroxide which contains appreciable amounts of HCl and FeCl_3 in the beginning. In fact we have observed that charge on

colloidal gold does not increase in the presence of small amounts of KCl as it does in the case of ferric hydroxide (unpublished results).

(2) As the charge on ferric hydroxide first increases on the addition of KCl, a greater amount of electrolyte will be required to coagulate the sol even when the charge on the colloid is initially small. We have observed that this effect becomes less marked as the purity of the colloid increases (unpublished results).

Conclusions.

From the foregoing considerations it would appear that there is nothing to warrant the view that charge and stability are not related with each other. The abnormal behaviour shown in any case can be traced to the part played by the similarly charged ions. It must, however, be pointed out at the same time that it is not safe to draw conclusions about the charge on colloidal particles from the results of stability as determined by flocculation values although in some cases flocculation values may serve a useful criterion for the same.

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A Study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene (-CH₂-) Group. Part IV.

By K. G. NAIK AND V. B. THOSAR.

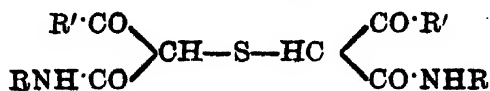
A close study of the reactions of thionyl chloride with organic compounds clearly shows that the course of reaction followed by thionyl chloride is entirely guided by the conditions of experiment in many cases. The reaction of thionyl chloride with phenols, phenetoles and alcohols might be cited as examples of this type. Generally in presence of anhydrous aluminium chloride, these compounds give rise to sulphides. But by slightly changing the conditions of the experiment, the same reaction can be made to follow a different course, as a result of which sulfoxides are obtained (Loth and Michaelis, *Ber.*, 1894, 27, 2540; Smiles and Rossignol, *J. Chem. Soc.*, 1908, 93, 745). Hence it was thought interesting to examine the course of the reaction followed by thionyl chloride when it reacts with substances containing a reactive methylene (-CH₂-) group in *cold ethereal solution*, although a similar reaction in *boiling benzene solution* had already resulted in the formation of sulfoxides (Naik, Desai and Parekh, *J. Indian Chem. Soc.*, 1930, 7, 137; Naik and Thosar, *ibid.*, 1932, 9, 127); and as will be seen from the experiments recorded in this paper this expectation is completely fulfilled.

Thionyl chloride was made to react with the following amides in presence of *cold* anhydrous ether.

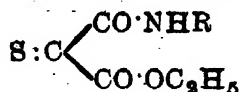
(1) Acetoacetanilide, (2) acetoacet-*o*-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet-*p*-toluidide, (5) acetoacet- β -naphthylamide, (6) acetoacet-1:3:4-xylidide, (7) malondi-*n*-propylamide, (8) malondi-isobutylamide, (9) malondiamylamide, (10) malondiheptylamide, (11) ethylmalon-*o*-tolylamate, (12) ethylmalon-*p*-tolylamate, (13) ethylmalon- β -naphthylamate, (14) ethylmalon-1:3:4-xylilamate, (15) ethylmalon-1:4:5-xylilamate.

The amides slowly went into solution, from which sulphides began to separate out, the reaction being complete after several days, the

time required depending upon the nature of the amide used. Amides (1) to (10) gave sulphides of the general constitution,



(where R=phenyl, tolyl, naphthyl, xylil or propyl groups and R' is either a CH_3 or $-\text{NHR}$ group); but in the case of amides (9) and (10) the reaction products were liquids which did not solidify even when placed in a freezing mixture. They will be worked up later. On the other hand the amates (11) to (15) gave sulphides of the formula

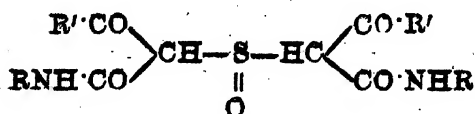


The above constitution of these sulphides follows from the following considerations:

(i) That the two hydrogen atoms are not supplied by the phenyl group, since (a) acetoacetic ester, which does not contain such a phenyl group reacts with thionyl chloride in a similar manner (Michaelis and Philips, *Ber.*, 1890, 23, 559); (b) malondi-*n*-propylamide containing no phenyl nucleus also reacts with thionyl chloride to give a similar compound.

(ii) That the hydrogen atoms eliminated are not those, which are originally attached to the nitrogen atom of $-\text{NHR}$ group, for (a) ethyl acetoacetate which does not contain such a hydrogen atom reacts similarly with thionyl chloride; (b) in case of malondi-*n*-propylamide which contains two such amido hydrogen atoms only one is replaced. On the supposition that the hydrogen atom of the $-\text{NHR}$ group is reactive both these hydrogen atoms must react.

Finally in order to establish that these compounds are not sulphoxides of the formula



advantage was taken of the fact that Michaelis and Philips had actually obtained a sulphide of acetoacetic ester by the action of thionyl chloride upon it (*loc. cit.*). As the conditions used by these authors were slightly different from those used here, thionyl chloride

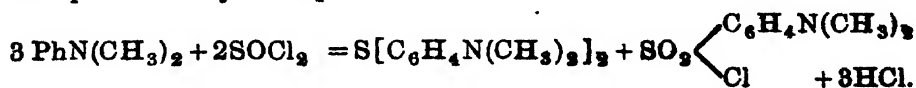
was made to react with acetoacetic ester under exactly the same conditions as were used here and it was found that the product obtained was identical with that obtained by the above authors. This sulphide of acetoacetic ester has been prepared by a host of workers from various sources so as to leave no doubt as to its constitution (Buchka, *Ber.*, 1885, 18, 2092; Delisle, *ibid.*, 1889, 22, 306; Schönbrodt, *Annalen*, 1889, 253, 198; Sprague, *J. Chem. Soc.*, 1891, 59, 329).

The reaction of thionyl chloride with amates (11) to (15) is also in favour of the sulphide constitution for the following reasons:

(i) These amates, when they were made to react with thionyl chloride in boiling benzene, where there is a greater possibility of the formation of sulphoxides, gave rise to liquid products (Naik, Desai and Parekh, *loc. cit.*).

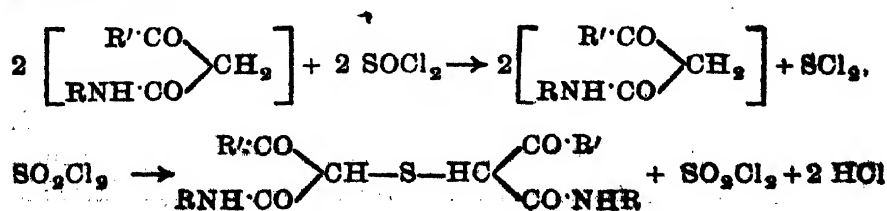
(ii) The reaction products obtained here are white crystalline substances, whereas the sulphoxides of the linking :C:S:O obtained till now are always coloured substances.

Michaelis and Philips (*loc. cit.*) hold that in such reactions, thionyl chloride behaves as if it were a mixture of sulphur dichloride and sulphuryl chloride, $2\text{SOCl}_2 \rightarrow \text{SCl}_2, \text{SO}_2\text{Cl}_2$, sulphur dichloride reacting with acetoacetic ester with the formation of the above sulphide. This view is further confirmed by the reaction of thionyl chloride with aromatic tertiary amines yielding two different products as represented by the equations:



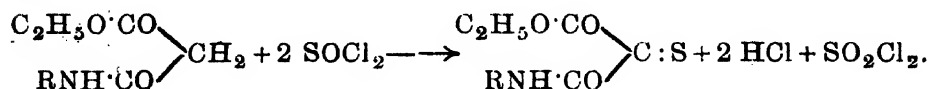
the second product being obtained by the action of sulphuryl chloride (SO_2Cl_2) on the amine (Michaelis and Godchaux, *Ber.*, 1890, 23, 553). The reaction of thionyl chloride with phenol also gives a sulphide together with other substances containing both sulphur and chlorine (Tassinari, *Gazzetta*, 1890, 20, 362).

The same explanation can very well be given in the reaction studied here.



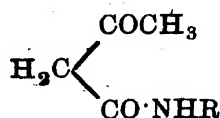
The course of the reaction followed by SO_2Cl_2 cannot be definitely ascertained here, as the mother liquor on evaporation gives only a semi solid mass, which it is proposed to work up later. In all probability the course followed by the reaction is different from that followed under ordinary conditions where chloro compounds are obtained (Naik and Shah, *J. Indian Chem. Soc.*, 1927, 4, 11). It is just possible that the catalytic action of thionyl chloride might again play its important part here and give rise to compounds of the type obtained in the case of tertiary amines and phenols.

The reaction in the case of amates (11) to (15) can be represented as

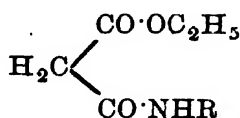


Such a course of reaction is not an abnormal one. Many instances can be cited where under similar conditions both the hydrogen atoms of the methylene group of the amates react, whereas usually only one hydrogen atom of the methylene group in the case of the aliphatic amides of malonic acid is found to react (Naik *J. Chem. Soc.*, 1921, 119, 379; West, *ibid.*, 1922, 121, 2196; Naik and Shah, *J. Indian Chem. Soc.*, 1930, 7, 111; Naik and Shah, *ibid.*, 1927, 4, 11; Norris and Thorpe, *J. Chem. Soc.*, 1921, 119, 1203). The course of reaction where only one hydrogen atom takes part, is explained by supposing that the second hydrogen atom becomes sluggish after the first is replaced by a substituent.

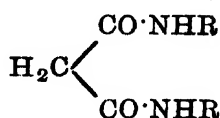
From the consideration of the time taken to complete the reaction (*vide experimental*) in a series such as,



(I)



(II)



(III)

the time required for the completion of the reaction in the case of the type (III) is longer than that required in the case of type (II), which in its own turn was found to be less reactive than type (I). This is quite in accord with the hypothesis put forward by Naik (*J. Chem. Soc.*, 1921, 119, 1166) and supported by the experimental work carried on in these laboratories since then. That the com.

pounds of type (II) are less reactive than those of type (I) follows from the fact that the total negativity of the adjoining carbonyl groups in type (II) is made smaller than that in type (I), by the replacement of a carbethoxy group in place of acetyl group, the other (-CONHR) group being common to all the three types. This total negativity is still further reduced in compounds of the type (III) where both the carbonyl groups are partially neutralised by the -NHR group and hence in this case the reactivity of the hydrogen atoms of the methylene group is the least and the time required for the completion of the reaction longest.

On examining the properties of these compounds it was found that the thio grouping (-S-) in these compounds is not so stable as the dithio grouping in the compounds obtained by Naik by the action of sulphur monochloride on substances containing the reactive methylene group (*J. Chem. Soc.*, 1921. 119, 1166, 1231). Thus, while the dithio grouping is quite unaffected by fuming nitric acid and silver nitrate, the thio grouping in these compounds is destroyed, giving rise to free sulphuric acid in the first case, and silver sulphide in the other. The sulphides derived from amates are still more unstable and are gradually decomposed on keeping for a long time.

EXPERIMENTAL.

Thiobisacetoacetanilide.—Thionyl chloride (2.5 g.) was added to pure dry acetoacetanilide (3.5 g.) suspended in dry ether (30 c. c.) in a conical flask tightly corked with a calcium chloride tube to avoid moisture and left at room temperature (28-30°). The amide slowly went in solution (3 hours) and the ethereal solution attained a rich red colour. On the next day white hexagonal plates began to separate out. After 3 days, when the reaction was complete the separated solid was filtered at the pump and washed with dry ether to free it from the excess of thionyl chloride. After crystallising it from a mixture of benzene and light petroleum (b. p. 50-60°) the substance was obtained in the form of white, hard, prismatic needles, m. p. 132°. But this substance was found to contain traces of hydrochloric acid from which, it could not be freed even on repeated crystallisations or keeping it in an alkali desiccator for a long time. The melting point also remained unchanged. Hence the substance was dissolved in benzene and boiled with a small amount of animal charcoal (0.2 g.)

under reflux for nearly 6 hours. The clear filtrate from animal charcoal was allowed to cool after adding an equal amount of dry light petroleum. The resulting product was now free from hydrochloric acid and was obtained in the form of white silky needles, m. p. 147° . It is interesting to note here that the impure compound had the same melting point (132°) in whatever conditions it was taken out of the reaction mixture. The analysis of the impure substance also amounted to nearly 1 mol. of hydrochloric acid in combination with 1 mol. of the sulphide.

The substance is readily soluble in benzene, sparingly so in chloroform, carbon tetrachloride, carbon disulphide and insoluble in petroleum ether and ether. (Found : N, 7.35; S, 7.90. $C_{20}H_{20}O_4N_2S$ requires N, 7.29; S, 8.33 per cent.).

All other sulphides were similarly prepared by treating the respective amides with thionyl chloride under the above conditions. A slight excess of thionyl chloride than required by equation was always necessary to compensate for the loss caused by gradual decomposition. All the sulphides except those obtained from amides had to be purified by boiling with animal charcoal for 6 hours. The results of these experiments are tabulated in Table I.

Hydrolysis of thiobisacetoacet- β -naphthylamide.—The compound (3 g.) was added to the solution of caustic potash (7 g.) in water (8 c. c.) and refluxed for 2 hours. The mixture was cooled and filtered. It was washed with cold water till it was free from alkali. The solid was crystallised from hot water, when characteristic rosy leaflets separated out, m. p. 111° . The substance was identified as β -naphthylamine and confirmed by mixed melting point. The filtrate was evaporated to dryness on a water-bath and the solid obtained was treated with hydrochloric acid when H_2S was found to evolve.

TABLE I.
[T=Thiobisaceto ; D=Thiobismalon ; E=Ethylmalon]

Name	Formula.	Appearance.	M. p.	Duration of reaction. (days)	Analysis Found.	Analysis Calc.
T-acetanilide	$C_{10}H_{11}O_4N_2S$	Silky needles	147°	$\frac{3}{8}$	S, 7.90 N, 7.8	8.3 p. c. 7.29
T-o-toluidide	$C_{12}H_{13}O_4N_2S$	Light flakes	160°	3	S, 7.6 N, 6.6	7.76 6.79
T-m-toluidide	$C_{12}H_{13}O_4N_2S$	Prismatic needles	104°	3	S, 7.53	7.76
T-p-toluidide	$C_{12}H_{13}O_4N_2S$	Silky needles	174°	3	S, 7.68	7.76
T-β-naphthylamide	$C_{22}H_{21}O_4N_2S$	Light tufts	186°	4	S, 6.26	6.61
T-(1:3:4)-xylil amide	$C_{14}H_{15}O_4N_2S$	Shining light tufts	139°	3	S, 7.32	7.21
D-di-n-propylamide	$C_{18}H_{29}O_4N_2S$	Short needles	123°	10	S, 8.05	7.95
D-di-t-butylamide	$C_{22}H_{29}O_4N_2S$	Light tufts	155°	12	S, 6.69	6.98
E-o-tolylamide sulphide	$C_{13}H_{13}O_3NS$	Small prisms	196°	6	S, 12.4	12.7
E-p-tolylamide sulphide	$C_{13}H_{13}O_3NS$	Hard needles	233°	6	S, 12.45	12.7
E-β-naphthylamide sulphide	$C_{23}H_{21}O_3NS$	Silky needles	208°	6	S, 11.01	11.14
E-1:3:4-xylilamide sulphide	$C_{13}H_{13}O_3NS$	Light tufts	176°	6	S, 11.79	12.08
E-1:4:5-xylilamide sulphide	$C_{13}H_{13}O_3NS$	Short crystals	187°	6	S, 11.88	12.08

The authors take this opportunity to express their gratitude to the Government of His Highness the Maharaja Geakwar of Baroda, for a grant which defrayed the expenses incurred in this work.

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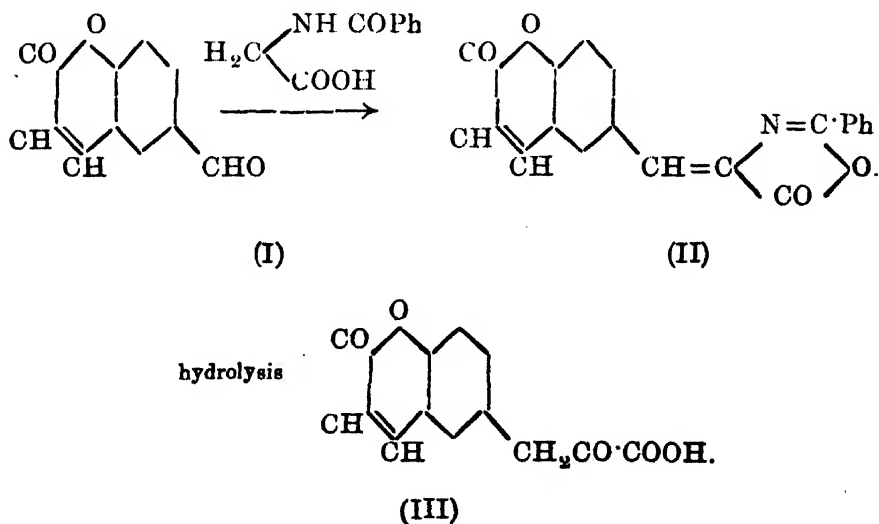
Received July 18, 1932.

Azlactone from 6-Aldehydocoumarin and its Condensation with some Aromatic Amines.

BY SANAT KUMAR BANERJEE.

The present investigation was undertaken with the object of synthesising phenanthracoumarin from 6-aldehydocoumarin, prepared by the application of the method adopted by Sen and Chakravarti (*J. Amer. Chem. Soc.*, 1928, **50**, 2428).

The aldehydocoumarin (I) has been condensed with hippuric acid, and the azlactone (II), obtained on alkaline hydrolysis gave the coumarin-6-pyruvic acid (III). The acid when oxidised with hydrogen peroxide in alkaline solution was expected to yield the coumarin-6-acetic acid. This being condensed with *o*-nitrobenzaldehyde by application of Pshorr's method (*Ber.*, 1896, **29**, 496) would yield phenanthracoumarin.



The hydrolysis of the azlactone was proceeded with difficulty. The product of hydrolysis was obtained as a tarry viscous mass and the yield was very small. The formation, however, of the expected keto-acid (III) as one of the products of the hydrolysis of the azlactone (II) has been qualitatively established by its condensation with

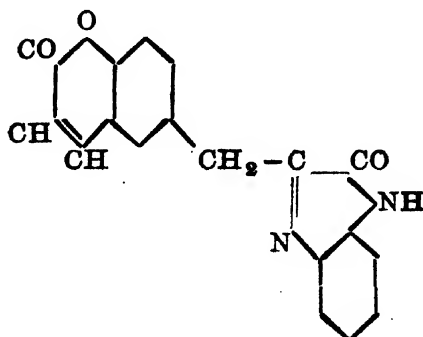
ortho-phenylenediamine(Gulland and Virden *J. Chem. Soc.*, 1928, 980).

The present work mainly deals with the properties of the azlactone and its condensation product with *p*-toluidine, α -naphthylamine and aniline. The condensation was effected by the method of Narang and Ray (*ibid.*, 1931, 976).

EXPERIMENTAL.

Preparation of the azlactone from 6-aldehydocoumarin.—A mixture of the aldehyde (10 g.), hippuric acid (10 g.), sodium acetate (5 g.) together with freshly distilled acetic anhydride (17 c.c.) was heated in a flask on a water-bath for $1\frac{1}{2}$ hours. The yellow mass so obtained was washed several times with alcohol and repeatedly boiled with a large volume of water to remove the excess of hippuric acid and filtered. The residual mass was boiled twice with considerable amount of 80 p.c. alcohol to remove the unreacted-upon aldehyde and it was finally crystallised from glacial acetic acid in lustrous yellow needles, m.p. 245° , yield 6 p.c. (Found: C, 71.8; H, 3.49; N, 4.4. $C_{19}H_{11}O_4N$ requires C, 71.92; H, 3.47; N, 4.41 per cent.).

Hydrolysis of the Azlactone and Isolation of Coumarin-6-pyruvic Acid in the form of Quinoxalino Compound.



The hydrolysis of the azlactone was effected by heating it with 10 p.c. caustic soda solution until the evolution of ammonia had ceased. The solution was then saturated with sulphur dioxide and filtered. The filtrate was boiled with hydrochloric acid when the keto-acid separated as a tarry mass which resisted all attempts for crystallisation. It however condensed with *o*-phenylenediamine,

when alcoholic solution of the two were shaken together. The quinoxalino-compound separated from acetic acid in light grey rhombic plates, m.p. 288-90°. (Found: C, 70.78; H, 3.95; N, 9.08. $C_{18}H_{12}O_3N_2$ requires C, 71.05; H, 3.61; N, 9.21 per cent.).

Condensation of the azlactone with p-toluidine.—Azlactone (9 g.) was heated with p-toluidine (3 g.) and a trace of copper-bronze at 150-60° for 2 hours. The cooled mass was extracted with hot acetic acid from which reddish brown silky crystalline plates of the compound having the formula $C_9H_5O_2CH:C(NH\cdot CPh)CONH\cdot C_6H_4\cdot CH_3$, separated. It was recrystallised from glacial acetic acid, m.p. 258°. (Found: C, 73.55; H, 5.21; N, 6.66. $C_{26}H_{20}O_4N_2$ requires C, 73.58; H, 4.95; N, 6.6 per cent.).

Condensation of the azlactone with α -naphthylamine.—The azlactone (9 g.) was similarly condensed with α -naphthylamine (4 g.) by heating the mixture at a temperature of 150° and the product was extracted with glacial acetic acid (charcoal) as yellowish needles of $C_9H_5O_2CH:C(NH\cdot CPh)CO\cdot NHC_{10}H_7$. (Found: C, 75.37; H, 4.7; N, 6.07. $C_{29}H_{20}O_4N_2$ requires C, 75.65; H, 4.35; N, 6.08 per cent.).

Condensation of the azlactone with aniline.—The azlactone was similarly condensed with aniline by heating equimolecular proportions of the two in the presence of a little copper-bronze at 130-40° for 1½ to 2 hours. The tarry viscous mass was treated with hot glacial acetic acid in which the compound was soluble. The acetic acid solution was boiled several times with charcoal and the clear solution on concentration yielded yellowish white needle shaped crystals of the compound. $C_9H_5O_2CH:C(NH\cdot CPh)CONHPh$, m.p. 178-80°. (Found: C, 72.98; H, 4.87; N, 6.79. $C_{25}H_{18}O_4N_2$ requires C, 73.17; H, 4.4; N, 6.83 per cent.).

In conclusion I wish to express my sincere thanks to Sir P. C. Rây for his kind interest in this investigation.

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Condensation of Chloral with 2-Hydroxy-*p*-toluic Acid and its Methyl Ether.

BY A. N. MELDRUM AND B. M. KAPADIA.

A synthesis of phenylacetic acids has been effected by means of three successive reactions, viz., (1) condensation of a benzoic acid with chloral (Fritch, *Annalen*, 1897, **296**, 356; 1898, **301**, 360), (2) the reduction of the -CH(OH)CCl_3 group to $\text{-CH}_2\text{CHCl}_2$ with zinc and acetic acid (Alimchandani and Meldrum, *J. Chem. Soc.*, 1921, **119**, 201), and (3) the hydrolysis and oxidation of $\text{-CH}_2\text{CHCl}_2$ to $\text{-CH}_2\text{COOH}$ with concentrated sulphuric acid (Alimchandani and Meldrum, *J. Indian Chem. Soc.*, 1929, **6**, 253).

The last mentioned reaction is not general. It is affected by the presence and position of other groups in the ring.

The present work was undertaken to study the condensation of 2-hydroxy-*p*-toluic acid with chloral and to extend the application of the method of obtaining phenylacetic acids.

2-Hydroxy-*p*-toluic acid when condensed with chloral in presence of sulphuric acid, yielded the 3-hydroxy-4-methyl- α -trichloromethyl phthalide (I). This was reduced with zinc and acetic acid when the phthalide ring opened and the 3-hydroxy-4-methyl-2 $\beta\beta$ -dichloroethylbenzoic acid (II) resulted. The compound (II) on hydrolysis and oxidation with concentrated sulphuric acid yielded the 2-hydroxy-3-methyl-6-carboxyphenyl-1-acetic acid (III).

The behaviour of the methyl ether of the acid was also examined.

On condensation with chloral and subsequent reduction with zinc and acetic acid it gave the 5-methoxy-4-methyl- α -trichloromethyl phthalide (VII) and 5-methoxy-4-methyl-2 $\beta\beta$ -dichloroethylbenzoic acid (VIII). The reduction product on treatment with concentrated sulphuric acid yielded the 3-methyl-4-hydroxy-6-carboxyphenyl-1-acetic acid (IX). Here concentrated sulphuric acid hydrolyses not only the group $\text{-CH}_2\text{CHCl}_2$ but also the methoxy group to the hydroxyl group. To confirm this (IX) was benzoylated.

These reactions have also been applied to the production of phenylbisacetic acid by further condensation of the phenylacetic acid (III) to (IV), subsequent reduction of (IV) and treatment of (V) with sulphuric acid. The 2-hydroxy-3-methyl-6-carboxyphenylene-1:5-bisacetic acid (VI) was finally obtained. The attempted condensation of (IX) with chloral was not successful. The product of the reaction does not contain chlorine but it is the 8-hydroxy-4:6-dimethylbenzoic acid (X).

The action of sodium hydroxide on the condensation products (I, IV, VII) has also been studied. With the hydroxytrichloromethyl phthalide alkali opens the ring and hydrolyses $-CCl_3$ to $-COOH$ group. Thus compound (I) yielded 2-hydroxy-6-carboxy-3-methylmandelic acid (Ia) and (IV) yielded 2-carboxy-3-carboxymethyl-4-hydroxy-5-methylmandelic acid (IVa).

But with the methoxytrichloromethyl phthalide (VII) the $-CCl_3$ group only is hydrolysed, the phthalide ring remaining intact so that 5-methoxy-4-methyl- α -carboxyphthalide (VIIa) was obtained.

The reason for the orientation assumed for the compounds mentioned must now be given.

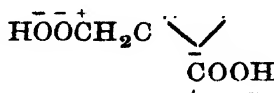
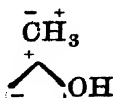
The *m*-linking of $-CHOH \cdot CCl_3$ group to the hydroxy or methoxy group has been ruled out of consideration for the following reasons. The compound (IX) was oxidised with potassium permanganate to 4-hydroxy-5-methylphthalic acid (IXa), m.p. 245° . This acid is not identical with known acid, 5-hydroxy-6-methylisophthalic acid (1:3), m.p. 270° (Jacobsen, *Ber.*, 1881, 14, 2115) where $COOH$ is in the *m*-position to hydroxyl group.

Hence the chloral molecule must have attached to the *o*- or *p*-position to the hydroxy or methoxy group.

The two phenylacetic acids (III and IX) are not identical. (III) melts at 213° whilst (IX) melts at 209° . The mixed m.p. is 200° . Hence again the chloral molecule attaches itself to different positions (*o* or *p*) depending whether the group present is hydroxyl or methoxyl. The substance (IX) was treated with chloral and sulphuric acid. With sulphuric acid (95 per cent.) the original product was recovered. But with the sulphuric acid (100 per cent.) the mixture after four days yielded two products, one with chlorine and the other without it. The first is a polymer of chloral, i.e., $(CCl_3CHO)_n$ but the second is the 8-hydroxy-4:6-dimethylbenzoic acid (X) (Gunter, *Ber.*, 1884, 17, 1608). This fixes the constitution of (IX).

The product (X) is formed by the elimination of carbon dioxide by the action of sulphuric acid (100 per cent.) in presence of chloral.

This elimination can be considered in the light of the "induced alternate polarity" principle of Vorländer. It has been found that the carbon dioxide is readily lost by a negative C-atom. Thus in (IX),



the methyl and carboxyl groups support one another in making the carbon atom which loses carbon dioxide negative.

Since the acids (III) and (IX) are different and since the chloral molecule $\text{CHOH} \cdot \text{CCl}_3$ in the methoxy compound is attached to the benzene ring in the *p*-position to the methoxy group, the linking in the hydroxy compound must be in the *o*-position.

EXPERIMENTAL.

3-Hydroxy-4-methyl- α -trichloromethyl phthalide, (I).—2-Hydroxy-*p*-toluic acid (10 g.), chloral hydrate (12 g.) and sulphuric acid (30 c.c., 95 p.c.) were shaken together to a clear solution. On the third day the mixture was poured over ice when a solid separated. It was crystallised from acetic acid and then from a mixture of acetone and petroleum ether in rectangular plates, m.p. 232° . (Found: Cl, 38.0. $\text{C}_{10}\text{H}_7\text{O}_3\text{Cl}_3$ requires Cl, 37.8 per cent.). It is soluble in alcohol, acetic acid, acetone, and insoluble in water, benzene, petroleum ether, toluene, chloroform.

Acetyl derivative crystallised from dilute alcohol, m.p. 142° . (Found: Cl, 38.0. $\text{C}_{12}\text{H}_9\text{O}_4\text{Cl}_3$ requires Cl, 32.9 per cent.).

Benzoyl derivative crystallised from methyl alcohol, m.p. 154° . (Found: Cl, 27.3. $\text{C}_{17}\text{H}_{11}\text{O}_4\text{Cl}_3$ requires Cl, 27.6 per cent.).

2-Hydroxy-6-carboxy-3-methylmandelic acid, (Ia).—The trichloromethyl phthalide (I) was heated on a water-bath with sodium hydroxide (200 c.c., 20 p.c.) for 3 hours. After cooling, it was acidified with dilute hydrochloric acid and extracted with ether. A thick oil was obtained which solidified on keeping in an alkali-desiccator. The solid mass was purified through its barium salt and then crystallised from a mixture of acetone and toluene. The acid can also be purified by distilling the thick oil at reduced pressure when the vapours condense to a yellow mass. This on crystallisation gave the pure product as needles, m.p. 115° . (Found: Eq. wt., 228.4; C, 58.0; H, 4.8. $\text{C}_{10}\text{H}_{10}\text{O}_6$ requires Eq. wt., 226.0; C, 58.1; H, 4.4 per cent.).

The *barium salt* is soluble in water. (Found: Ba, 37.7. $C_{10}H_8O_6$ Ba requires Ba, 38.0 per cent.). The substance is soluble in alcohol, acetone, sparingly soluble in benzene, and toluene, insoluble in petroleum ether and chloroform.

3-Hydroxy-4-methyl-2-ββ-dichloroethylbenzoic acid, (II).—The trichloromethyl phthalide (I) (10 g.) was dissolved in acetic acid. Zinc dust (7.5 g.) was then added in small quantities while the mixture was automatically shaken. After 3 hours the mixture was filtered and the filtrate diluted with water. A white light substance separated. This was collected and crystallised from benzene in feathery concentric needles, m.p. 184°. (Found: Eq. wt., 247.0; Cl, 28.3. $C_{10}H_{10}O_3Cl_2$ requires Eq. wt., 249.0; Cl, 28.5 per cent.). The substance is soluble in acetic acid, acetone, alcohol, sparingly soluble in ether, toluene, benzene and insoluble in petroleum ether.

Acetyl derivative crystallised from a mixture of petroleum ether and acetone, m.p. 185° (mixed with starting substance, m.p. 169°). (Found: Cl, 24.4. $C_{12}H_{12}O_4Cl_2$ requires Cl, 24.4 per cent.).

Benzoyl derivative crystallised from benzene, m.p. 140°. (Found: Cl, 20.3. $C_{17}H_{14}O_4Cl_2$ requires Cl, 20.1 per cent.).

Barium salt crystallised with 3 molecules of water of crystallisation. [Found: Ba, 19.7. $(C_{10}H_8O_3Cl_2)_2$ Ba, $3H_2O$ requires Ba, 20.0 per cent.].

2-Hydroxy-3-methyl-6-carboxyphenyl-1-acetic acid, (III).—The acid (II, m.p. 184°) (10 g.) was added to concentrated sulphuric acid (30 c.c., 95 p.c.) in very small quantities. The substance changed to yellow colour and hydrogen chloride gas was evolved. On heating on the water-bath, the whole turned to brown sticky mass, which was filtered through flannel and transferred to a porous plate. It was dried in an alkali-desiccator. The dry mass was crystallised from water three times in square plates, m.p. 213°.

The sulphuric acid mother liquor was diluted and extracted with ether yielding further quantity of the substance. (Found: Eq. wt., 209.8; C, 57.1; H, 4.7. $C_{10}H_{10}O_5$ requires Eq. wt., 210.0; C, 57.1; H, 4.7 per cent.). The substance is very soluble in acetic acid, alcohol, acetone, ether, water, slightly soluble in benzene, toluene, petroleum ether, chloroform.

Barium salt crystallised with $1H_2O$. (Found: Ba, 37.6. $C_{10}H_8O_5Ba$ requires Ba, 37.8 per cent.).

Benzoyl derivative was prepared by the pyridine method. It was isolated by extraction with ether and repeatedly crystallised from

hot water in feathery needles, m.p. 126° . (Found: Eq. wt., 818.8. $C_{17}H_{14}O_6$ requires Eq. wt., 814).

The *methoxy* derivative was prepared by the methyl sulphate method, crystallised from dilute acetic acid and recrystallised from a mixture of chloroform and acetone in prismatic plates, m.p. 206° . (Found: Eq. wt., 225.6. $C_{11}H_{12}O_5$ requires Eq. wt., 224).

The *acetyl* derivative was prepared using acetic anhydride. The product was extracted with ether, and crystallised from water, m.p. 110° . (Found: Eq. wt., 251.8. $C_{12}H_{12}O_6$ requires Eq. wt., 252).

2-*Hydroxy-3-methyl-6- α -trichloromethylphthalide-phenylacetic acid*, (IV).—The phenylacetic acid (III, m.p. 213°) (6 g.) and freshly distilled chloral (9 g.) were mixed with sulphuric acid. After 4 days the mixture was poured over crushed ice. The slightly yellow powder was collected, crystallised from acetic acid and recrystallised from acetone and toluene in concentric needles, m.p. 249° . (The yields are improved by using 100 p. c. sulphuric acid from 21 p. c. to 47 p. c.).

The same substance can be obtained directly from (II). The sulphuric acid acts as the condensing agent as well as hydrolysing and oxidising agent. (But the yields are poor and the purification is tedious). (Found: Cl, 31.0. $C_{12}H_9O_5Cl_3$ requires Cl, 31.3 per cent.).

2-*Carboxy-3-carboxymethyl-4-hydroxy-5-methylmandelic acid*, (IVa).—It was prepared by the action of sodium hydroxide on (IV). The acid was isolated by extracting with ether and crystallised from ether in rectangular plates, m.p. 246° . (Found: Eq. wt., 281.5. $C_{12}H_{12}O_8$ requires Eq. wt., 284).

2-*Hydroxy-3-methyl-5- $\beta\beta$ -dichloroethyl-6-carboxyphenyl-1-acetic acid*, (V).—The trichloromethylphthalide-phenylacetic acid (IV, m.p. 249°) (10 g.) was dissolved in glacial acetic acid (300 c.c.) by heating. Zinc dust (35 g.) was added in small quantities at a time to the solution. After heating for 8 hours the mixture was filtered off from unchanged zinc and zinc acetate. The filtrate was then evaporated on the water-bath. The sticky yellowish syrup-like substance was kept in an alkali desiccator for 8 days. The mass was then treated with a small quantity of water and the white solid obtained was collected and dried. It was crystallised from water and recrystallised from a mixture of toluene and acetone in small white needles, m. p. 208.05° . (Found: Cl, 22.9. $C_{12}H_{12}O_5Cl_2$ requires Cl, 23.1 per cent.). The substance is soluble in acetic acid, alcohol, acetone, insoluble in ether, toluene, benzene, chloroform, petroleum ether.

2-Hydroxy-3-methyl-6-carboxyphenylene-1:5-bisacetic acid, (VI) was prepared by the action of sulphuric acid on the compound (V) (m.p. 203-205°) and crystallised from a mixture of toluene and acetone, m.p. 220°. (Found: Eq. wt., 265.2. $C_{12}H_{12}O_7$ requires Eq. wt., 268.0). The substance is soluble in acetone, alcohol, water (hot), insoluble in benzene, chloroform, sparingly soluble in petroleum ether.

5-Methoxy-4-methyl- α -trichloromethyl phthalide, (VII).—2-Methoxy-*p*-toluic acid (m.p. 164°) (10 g.) and chloral hydrate (10 g.) were mixed with sulphuric acid (50 c.c.). On shaking the substance went into solution. After 3 days a white mass separated. The whole mixture was then poured over crushed ice. The white pasty mass was allowed to remain in the mother liquor for 12 hours when it set to a hard mass. This was crystallised from acetic acid and recrystallised from dilute alcohol in rectangular plates, m.p. 132°. (Found: Cl, 35.8. $C_{11}H_9O_3Cl_3$ requires Cl, 36.0 per cent.). The substance is soluble in acetic acid, alcohol, sparingly soluble in ether, petroleum ether, chloroform, toluene, benzene.

5-Methoxy-4-methyl- α -carboxyphthalide, (VIIa).—5-Methoxy-4-methyl- α -trichloromethyl phthalide (VII, m.p. 132°) was heated with sodium hydroxide (100 c.c., 20 p.c.). The brown mass obtained by acidifying the solution mixture was crystallised from a mixture of acetone and toluene in rectangular plates, m.p. 222°. (Found: Eq. wt., 220; C, 59.3; H, 4.5. $C_{11}H_{10}O_5$ requires Eq. wt., 222.0; C, 59.4; H, 4.5 per cent.).

Barium salt crystallised with 2 molecules of water of crystallisation. [Found: Ba, 22.1. $(C_{11}H_9O_5)_2Ba \cdot 2H_2O$ requires Ba, 22.3 per cent.].

5-Methoxy-4-methyl-2- $\beta\beta$ -dichloroethylbenzoic acid, (VIII).—5-Methoxy-4-methyl- α -trichloromethyl phthalide (VII) (m.p. 132°) was reduced with zinc and acetic acid. The white mass obtained by diluting the acetic acid filtrate was crystallised from dilute acetic acid and recrystallised from toluene in fine clusters of feathery needles, m.p. 195°. (Found: Eq. wt., 259.7; Cl, 26.8. $C_{11}H_{12}O_3Cl_2$ requires Eq. wt., 263.0; Cl, 27.0 per cent.). The substance is soluble in acetic acid, acetone, benzene (hot), toluene (hot), ether, insoluble in petroleum ether.

Barium salt is insoluble in water. [Found: Ba, 20.5. $(C_{11}H_{11}O_3Cl_2)_2Ba$ requires Ba, 20.7 per cent.].

3-Methyl-4-hydroxy-6-carboxyphenyl-1-acetic acid, (IX).—The reduction product (VIII) was powdered and was added in small quantities to concentrated sulphuric acid. Hydrogen chloride was copiously evolved. The reaction mixture was properly shaken and heated and after 6 hours it was poured over ice-water when a yellow mass separated. Crystallised from acetic acid and recrystallised from methyl alcohol in prismatic plates, m.p. 209° (m.p. 200° in mixture with 2-hydroxy-3-methyl-6-carboxyphenyl-1-acetic acid, III). (Found: Eq. wt., 210.0; C, 56.9; H, 4.5. $C_{10}H_{10}O_5$ requires Eq. wt., 210.0; C, 57.1; H, 4.7 per cent.).

Barium salt is insoluble in water. (Found: Ba, 39.7. $C_{10}H_8O_5Ba$ requires Ba, 39.8 per cent.).

Benzoyl derivative crystallised from methyl alcohol in needles, m.p. 170° . (Found: Eq. wt., 312.6. $C_{17}H_{14}O_6$ requires Eq. wt., 314.0).

4-Hydroxy-5-methylphthalic acid, (IXa).—The phenylacetic acid (IX, m.p. 209°) (4 g.) was dissolved in dilute potassium hydroxide solution (200 c.c., 5 p. c.) and the liquid heated on the water-bath. Potassium permanganate (300 c.c., 2 p. c.) was slowly added. After heating for 5 hours the mixture was filtered from manganese dioxide, concentrated to small volume and acidified with sulphuric acid. The white mass that precipitated was washed several times and crystallised five times from hot water, m.p. $244-45^{\circ}$. (Found: Eq. wt., 195.7; C, 54.8; H, 4.1. $C_9H_8O_5$ requires Eq. wt., 196.0; C, 55.0; H, 4.0 per cent.).

Barium salt is insoluble in water. (Found: Ba, 41.2. $C_9H_6O_5Ba$ requires Ba, 41.4 per cent.).

3-Hydroxy-4: 6-dimethylbenzoic acid, (X).—The mixture of the phenylacetic acid (IX, m.p. 209°) (8 g.) and chloral (12 g.) with sulphuric acid (225 c.c., 100 p. c.) was kept for 8 days. During this time continual effervescence was observed. A reddish yellow substance separated on pouring over ice. This was collected and was found to be a mixture of two compounds A and B.

Separation of A.—The reddish yellow mass was dissolved in a small quantity of acetic acid (hot). On keeping a white mass settled down. This was collected, washed and dried, m.p. 130° . (The acetic acid mother liquor was kept for further treatment). The mass, (m.p. 130°) was dissolved in methyl alcohol which deposited a substance, m.p. 165° . This was crystallised from acetic acid and finally from toluene in concentric needles, m.p. $170-71^{\circ}$. (Found:

Eq. wt., 166.9 ; C, 64.9 ; H, 6.0. $C_9H_{10}O_3$ requires Eq. wt., 166.0 ; C, 65.0 ; H, 6.0 per cent.). The substance is soluble in alcohol, acetic acid, toluene (hot), benzene (hot), acetone, insoluble in petroleum ether, chloroform. *Barium salt* is insoluble in water. [Found : Ba, 29.2. $(C_9H_9O_3)_2Ba$ requires Ba, 29.4 per cent.]. *Acetyl derivative* crystallised from a mixture of acetone and petroleum ether in needles, m.p. 134°. (Found : Eq. wt., 206.5. $C_{11}H_{12}O_4$ requires Eq. wt., 208).

Separation of B [polymer of chloral $(CCl_3CHO)_n$].—The acetic acid mother liquor from A was diluted with water. A pasty mass was obtained. The methyl alcohol and toluene mother liquors also yielded a yellow powder. All these substances were dissolved in acetic acid (hot) which deposited a mass, m.p. 115°. This was crystallised from methyl alcohol and finally from petroleum ether in rectangular plates, m.p. 120°. The results of six chlorine estimations were not in close agreement only two are given. [Found : Cl, 71.47, 72.56. $(CCl_3CHO)_n$ requires Cl, 72.2 per cent.]. The substance is very soluble in alcohol, acetic acid, acetone, benzene, toluene, sparingly soluble in petroleum ether.

The authors are grateful to Dr. T. S. Wheeler, Principal, Royal Institute of Science, Bombay and to Mr. R. C. Shah, M.Sc., A.I.I.Sc., for their interest in the work.

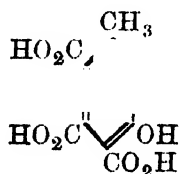
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ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

Received May 12, 1932.

Synthesis of 1:2:7-Trihydroxy-5-methylanthrone-8-carboxylic Acid.

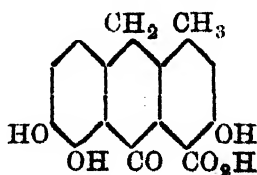
BY PRAFULLA KUMAR PAUL.

In course of oxidation of coccinine (*Annalen*, 1916, **399**, 1) the polyhydric phenol residue is lost, with the production of cochenillic acid, to which the following constitution has been assigned by Dimroth from analytical standpoint and some of the reactions of the acid.



It was therefore of some interest to attempt synthesis of anthrones composed of a *m*-cresotinic acid residue and a polyhydric phenol residue, which on oxidation may possibly produce cochenillic acid and thus definitely settle its constitution.

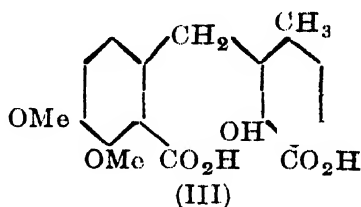
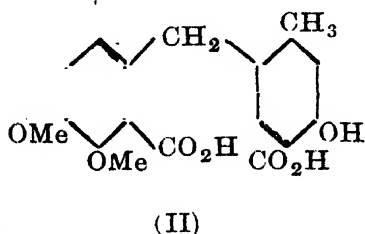
With this end in view 3:4:5-trimethoxy-1:2-phthalide (Alimchandani and Meldrum, *J. Chem. Soc.*, 1920, **117**, 964), 6-methyl-3:5-dimethoxy-1:2-phthalide (Mitter, Sen and Paul, *J. Indian Chem. Soc.*, 1927, **4**, 536) and 5:6-dimethoxy-1:2-phthalide (meconine) were condensed with ethyl methoxy-*m*-cresotinate in presence of aluminium chloride (King, *J. Amer. Chem. Soc.*, 1927, **49**, 563) and partially demethylated benzylbenzoic acid derivatives were obtained. The yield of these condensation products, was generally low, and they hardly undergo ring closure to yield anthrone derivatives. Only a very poor yield of anthrone derivative could be obtained from the condensation product of meconine and ethyl methoxy-*m*-cresotinate which on demethylation with hydrobromic acid in glacial acetic acid gave the following compound.



(I)

The quantity of 1:2:7-trihydroxy-5-methylanthrone-8-carboxylic acid (I) obtained was very small and no more than 0.5 g. of the substance could be subjected to the oxidising action of alkaline hydrogen peroxide (*Ber.*, 1909, **42**, 1625) from which no definite result could be obtained and so the following alternative scheme for the synthesis of (I) was adopted.

Opianic acid was condensed with ethyl-*m*-cresotinate in presence of 85 per cent. sulphuric acid (Jacobson and Adam, *J. Amer. Chem. Soc.*, 1925, **47**, 2011). The condensation product was then hydrolysed with 10 per cent. alcoholic potash and the product of hydrolysis completely reduced with zinc dust and 10 per cent. caustic soda solution. The benzylbenzoic acid derivative thus produced may have the alternative formulae given below.



The neutral methoxymethyl ester was prepared and found to be identical with that prepared from the condensation product of meconine with ethyl methoxy-*m*-cresotinate, where condensation takes place mainly at the *para*-position to the OMe group of ethyl methoxy-*m*-cresotinate, as is evident from the ring closure of the benzylbenzoic acid derivative already mentioned. The identity of the benzylbenzoic acid derivatives prepared by alternative methods, leaves no room for doubt as to the constitution of the product being (II).

A proper condition for ring closure of (II) to yield anthrone derivative has not yet been found and all attempts to that end have so far failed.

EXPERIMENTAL.

Condensation of meconine with ethyl methoxy-m-cresotinate.—Meconine (10 g.) and ethyl methoxy-*m*-cresotinate (10 g.) were dissolved in chloroform (50 c. c.) in a R. B. flask fitted up with a reflux condenser, and anhydrous aluminium chloride

(10 g.) was added in two instalments and heated on the water-bath for 6 hours, when the reaction mixture turned into a deep brown homogeneous solution. A further quantity of aluminium chloride (15 g.) was then added and the heating continued for a further period of 20 hours. The reaction product was found to be deep red solid mass, which was then decomposed with ice-cold dilute hydrochloric acid and steam distilled to ensure the decomposition of the aluminium compound formed during the reaction. The reaction product was then cooled and extracted with ether and the ethereal extract washed repeatedly with sodium bicarbonate solution. The bicarbonate-wash on acidification with hydrochloric acid yielded the condensation product as a brown solid, which crystallised from glacial acetic acid, m. p. 207° . [Found: C, 61.16; H, 5.22; OMe, 9.60. $C_{17}H_{16}O_7$ requires C, 61.45; H, 4.82; OMe (Mono), 9.33 per cent.].

Neutral methoxymethyl ester of the above benzylbenzoic acid derivative was prepared by heating the same (1.5 g.) with sodium (0.5 g.) in methyl alcohol and methyl iodide (4 g.) in a sealed tube for 2 hours at 100° . It crystallised from methyl alcohol in stout needles, m. p. $98-99^{\circ}$. (Found: C, 64.57; H, 6.34. $C_{21}H_{24}O_7$ requires C, 64.94; H, 6.18 per cent.).

Ring closure of the condensation product.—The condensation product was dissolved in chemically pure sulphuric acid (5 c.c.) to a deep red solution, and kept for 12 hours at ordinary temperature, when the colour of the solution changed to dirty green. It was then warmed at $65-70^{\circ}$ for 10 minutes, when the colour changed, first from bottle green to deep green, then blue and ultimately bluish violet, when it was cooled and poured on to crushed ice. The solid reaction product which was black with a violet tinge was separated, dried and dissolved in ethyl acetate. The deep red ethyl acetate extract was made free from tarry impurities by precipitating them with petroleum ether, when a beautiful scarlet solution was obtained, which on concentration gave the reaction product as a pink powder. It crystallised from a large volume of benzene with a few drops of ethyl acetate in needles, m. p. 225° . (Found: C, 64.57; H, 5.0. $C_{17}H_{14}O_6$ requires C, 64.97; H, 4.46 per cent.).

1:2:7-Trihydroxy-5-methylanthrone-8-carboxylic acid, (1).—The product of ring closure (1 g.) (m. p. 225°), as described above was demethylated by heating with hydrobromic acid in glacial acetic

acid (15 c.c.) under reflux for 3-4 hours. The acetic acid was removed from the reaction product under reduced pressure in a desiccator over caustic potash, when the compound was obtained mixed with some tarry matter, which was removed by fractional precipitation with benzene, from an ethyl acetate solution of the reaction product. The compound thus obtained was dissolved in least quantity of glacial acetic acid and allowed to stand in a desiccator over caustic potash when it was obtained in crystalline condition, m. p. 255° (decomp.) with previous blackening between $245-50^{\circ}$. It dissolves in alkali with a violet coloration which changes ultimately to deep brown. (Found: C, 63.84; H, 4.25. $C_{16}H_{21}O_6$ requires C, 64.0; H, 4.0 per cent.).

Condensation of opianic acid with ethyl m-cresotinate.—Opianic acid (14 g.) was intimately mixed with ethyl *m*-cresotinate (12 g.) and to the mixture sulphuric acid (85 p. c., 40 c. c.) was added, when a light brown homogeneous solution resulted with slight rise in temperature. It was then allowed to stand at ordinary temperature for 6-7 hours and diluted with water, when the condensation product separated. It was then extracted with ether, the ethereal extract washed with sodium bicarbonate solution, dried with calcium chloride and ether allowed to evaporate when the reaction product was obtained as a solid, crystallising from alcohol in needles, m. p. 93° . (Found: C, 64.71; H, 5.71. $C_{20}H_{20}O_7$ requires C, 64.52; H, 5.38 per cent.).

The corresponding acid was obtained by hydrolysing the condensation product by heating with 5 times the required quantity of alcoholic potash under reflux on a water-bath for 3 hours. The reaction mixture was then diluted with half its volume of water, alcohol driven off on a water-bath, cooled and acidified with hydrochloric acid, when a white solid separated. It crystallised from acetic acid, m. p. 255° . (Found: C, 62.44; H, 4.9. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.65 per cent.).

The same compound was obtained by direct condensation of opianic acid with *m*-cresotinic acid in presence of 85 p. c. sulphuric acid but it is not advantageous owing to the difficulty of separation of the required condensation product from the unreacted acids.

Benzylbenzoic acid derivative, (II).—The reduction of the preceding compound (m. p. 255°) to the corresponding benzylbenzoic acid derivative was achieved by boiling the same (10 g.) with fresh zinc dust (80 g.) and caustic soda solution (10 p. c., 200 c. c.) under

vigorous mechanical stirring under reflux for 20 hours. When the reaction was over, the reaction mixture was cooled and filtered, the filtrate on acidification with hydrochloric acid gave the reduction product as a pasty mass, which soon solidified. It crystallised from glacial acetic acid in prisms, m. p. 183° . (Found: C, 62.05; H, 5.52. $C_{18}H_{18}O_7$ requires C, 62.43; H, 5.2 per cent.).

A neutral methoxymethyl ester of the benzylbenzoic acid derivative (m. p. 183°) was prepared in a similar way as that of the condensation product of meconine with ethyl methoxy-*m*-cresotinate. It crystallised from methyl alcohol, m. p. 101° . (Found: C, 64.82; H, 6.45. $C_{21}H_{24}O_7$ requires C, 64.94; H, 6.18 per cent.). The identity of the two neutral methoxymethyl esters was ensured by an observation of no depression in the melting point of an intimate mixture of the two.

*Condensation of 3:4:5-trimethoxy-1:2-phthalide with ethyl methoxy-*m*-cresotinate.*—Equimolecular quantities of 3:4:5-trimethoxy-1:2-phthalide and ethyl methoxy-*m*-cresotinate in chloroform solution were treated with aluminium chloride, the procedure being the same as that used in the case of the condensation of meconine with ethyl methoxy *m*-cresotinate. The compound crystallised in beautiful needles from benzene, m. p. 137° . (Found: C, 59.27; H, 5.11. $C_{18}H_{18}O_8$ requires C, 59.68; H, 4.97 per cent.).

*Condensation of 6 methyl-3:5 dimethoxy-1:2-phthalide with ethyl methoxy-*m*-cresotinate.*—The condensation of equimolecular quantity of the phthalide and ethyl methoxy-*m* cresotinate was carried out in chloroform solution in presence of aluminium chloride as usual, only the heating on the water-bath was prolonged to 35 hours. The substance crystallised from water with a little alcohol in beautiful white stout needles, m. p. 203.04° . (Found: C, 62.62; H, 5.68. $C_{18}H_{18}O_7$ requires C, 62.43; H, 5.2 per cent.).

My grateful thanks are due to Prof. P. C. Mitter for his kind interest in the investigation and for his giving me every facility to carry out the work.

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Peroxidases. Part II. The Influence of the Concentration of Substrate (Hydroquinone), of Hydrogen Peroxide, P_H and other Factors on the Activity of the Peroxidase of Chow Chow (*Sechium Edule*).

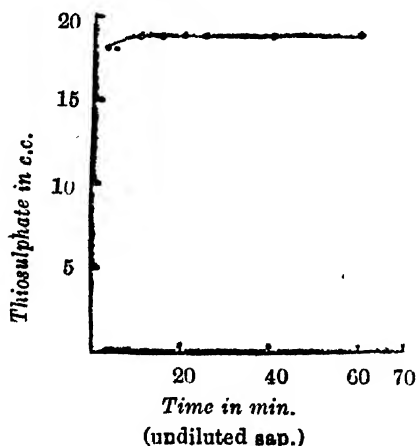
BY BIMAN BIHARI DEY AND MAYAVARAM VASUDEVA SITHARAMAN.

In the present paper several of the important factors which influence the activities of peroxidases have been studied in detail, the peroxidase activities being determined by the method described previously (*J. Indian Chem. Soc.*, 1931, **8**, 479). The vegetable commonly known as Chow Chow (*Sechium Edule* S. W., N. O. *Cucurbitaceæ*), is found to be extraordinarily rich in this enzyme, and all experiments recorded in this paper have been carried out with an enzyme extract prepared from this particular vegetable. Several attempts were made to prepare the enzymes both from the Jhinga (*Luffa acutangula*) and the chow chow fruits in as pure a condition as possible by the usual methods described by Willstätter and Stoll (*Annalen*, 1918, **416**, 21), but a certain amount of rotting invariably set in during the preliminary process of soaking the thin slices of the vegetables in flowing water for several days, as recommended by these authors, for the purpose of removing the simpler products by dialysis through the cell walls themselves. A material which may be considered to be an extract of the oxidising enzymes practically free from all foreign matter, prepared by the method described below, has, however, been found to be very suitable for the purposes of these investigations. The fresh vegetable, cut into very thin slices, is washed in running water for a few hours, and then made into pulp with an ordinary mutton chopper tinned on the inside and paraffined all over to prevent the sap from coming into contact with the metal. The pulp is gently squeezed through muslin bags, an average chow chow fruit, weighing about 250 g., yielding in this way 120-140 c.c. of a nearly colourless, and somewhat turbid liquid. This was now dialysed through a parchment bag in a tall beaker at 10°, in a refrigerator, the water to which a few drops of toluene had been added being frequently replaced. The operation normally required 4

days at the end of which period the dialysed sap became clear and its osmotic pressure had greatly diminished. It was now centrifuged to remove all suspended particles, and finally filtered through paper pulp into a bottle containing a few drops of toluene, and preserved in the refrigerator. An extract prepared in this manner retained its peroxidase activity perfectly unimpaired and gave the same titre value with lecinorm: thiosulphate, even at the end of one month as when it was freshly made. The pH of this liquid, determined in all cases with the quinhydrone electrode, usually ranged between 4.5 and 4.6, but in rare instances it has been found to go down as low as 4.33 or rise as high as 4.86.

The extract, in the case of chow chow, is found to contain the enzymes in a very concentrated form, and the normal reaction with hydroquinone proceeds so rapidly that equilibrium is attained almost immediately. * The undiluted sap could not therefore be used for the purpose of studying the kinetics of this oxidation reaction, and a few preliminary experiments had to be made to determine the precise concentration and volume of the enzyme solution which was most suitable for these studies. The course of the reaction was followed with (a) the undiluted sap, (b) the sap diluted with an equal volume of water, (c) sap diluted with three times its volume of water and (d) sap diluted with seven times its volume of water, corresponding respectively to the original, half, one-fourth, and one-eighth of the concentration of the enzyme in the sap.

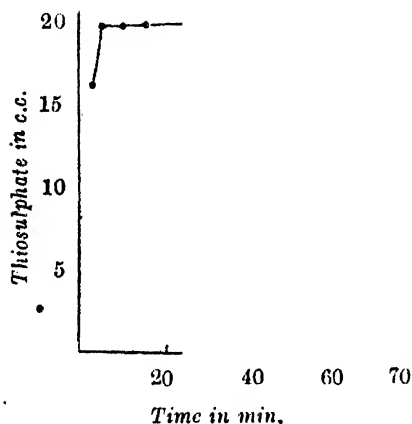
FIG 1.



* In this preparation, the peroxidase was not contaminated with oxygenase as no oxidation was found to occur in the absence of hydrogen peroxide.

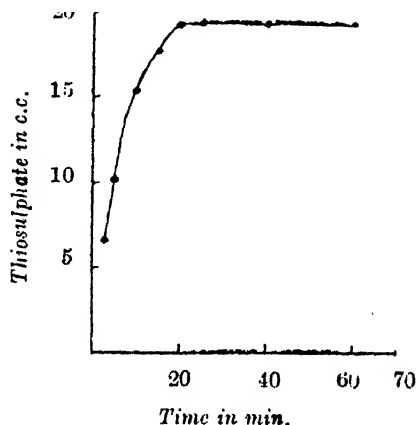
It would be seen from the results given in Tables I and II that a dilution corresponding to a fourth of the enzyme concentration of the undiluted sap works most satisfactorily. A 15 minutes reaction period was found to be the most suitable, while a volume of 5 c.c. of the dilute enzyme solution which produced the maximum effect under the conditions of our experiments, was chosen in all cases. All reactants were measured directly from a refrigerator maintaining a constant temperature of 13°. The results are shown in Tables I and II and in Fig. 1, 2 and 3.

FIG. 2.



(Sap diluted with its own
vol. of water.)

FIG. 3.

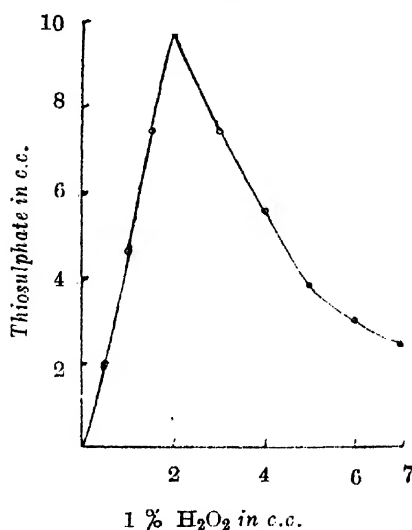


(Sap diluted with 3 times
its vol. of water.)

Effect of the hydrogen peroxide concentration on peroxidase activity.—Bach (*Ber.*, 1904, **37**, 3737), Willstätter and Weber (*Annalen*, 1926, **449**, 175) and Mann (*Biochem. J.*, 1931, **25**, 918) have shown that excess of hydrogen peroxide inhibits the activity of the peroxidases, and in larger quantities, destroys it altogether, and in our experiments with the peroxidase of *Luffa acutangula* described previously, we have been able to confirm these conclusions. It is, therefore, essential to determine carefully the proper concentration of hydrogen peroxide to be employed in each experiment which is calculated to prevent any destruction of the enzyme, and at the same time to produce the maximum effect. Several experiments were made in which the concentration of H_2O_2 was varied, while all the other factors were kept constant. The precipitated quinhydrone was collected on a coarse Jena sintered glass filter and estimated volumetrically according to the usual method. From the

results given in Table III and in Fig. 4, it will be evident that under the conditions of our experiments, the maximum activity is

FIG. 4.

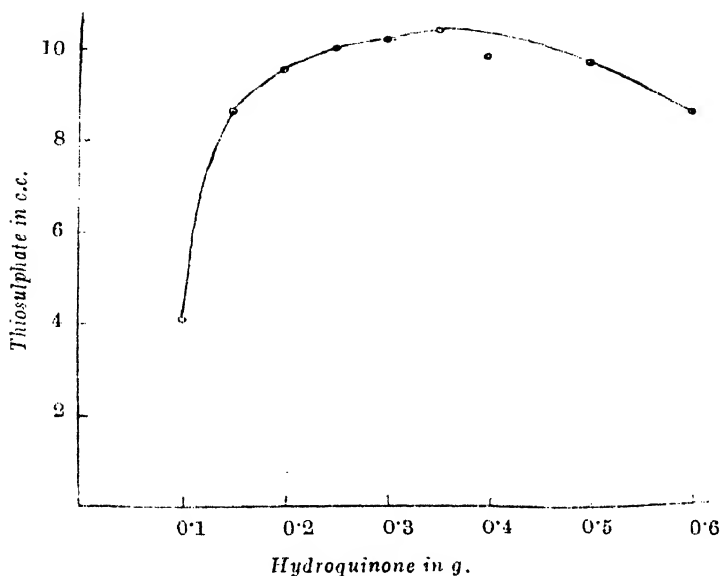


attained when the amount of hydrogen peroxide added is 2 c.c. of 1 p. c. strength (0.02 g. in 13 c.c. of reaction mixture), and this concentration of H_2O_2 was therefore adhered to in all the subsequent experiments.

Effect of the concentration of substrate at constant pH.—In the course of an interesting series of experiments of an allied type on the peroxidase of horse-radish roots, Getchell and Walton (*J. Biol. Chem.*, 1931, 91, 419) have shown that at pH 6 and with pyrogallol substrate, the concentration of maximum activity is 10 dg. per 100 c.c., other conditions, *c. g.*, strength of the enzyme solution, etc., remaining unaltered. The usual curve with mg. of purpurogallin plotted as ordinate and dg. of pyrogallol plotted as abscissa, shows a peak at 10 dg. and falls off rapidly after the concentration has reached this limit. On account of the limited solubility of hydroquinone, it was not possible to carry on our experiments beyond a concentration of 4.5 per cent. A citrate buffer of pH 5.2, was used and a constant volume was added for each experiment. The hydroquinone was weighed out in each case, instead of adding it in solution, and the total volume of the reaction mixture was thus kept constant. The curve does not show any well defined peak, and the activity seems to remain constant when the concentration of

the substrate is between 0.25 and 0.35 at the total constant volume of 13 c.c. (cf. Table IV and Fig. 5).

FIG. 5.



Activity-ph relationship.—McIlvaine's citrate buffer, providing a convenient range from pH 2.2 to pH 8.0, was prepared by using the purest citric acid crystals and sodium phosphate (Sørensen's $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$). 5–6 C.c. of the buffer were measured into a 50 c.c. beaker, and 2 c.c. of 1 per cent. H_2O_2 , 0.3 g. of hydroquinone and 5 c.c. of the enzyme solution successively added, the total volume being kept constant in each case. The reaction was stopped by adding 2 c.c. of 2N-HCl. With hydroquinone substrate, the activity is perceptible even in $N/10$ solutions of HCl with a pH of about 1.07. The optimum pH for the peroxidase of horse-radish has been given as 7 when pyrogallol is used as the substrate, while with guaiacol it lies between 5 and 5.2, and with *o*-cresol, between 3.5 and 3 (cf. Bansi and Ucko, *Z. physiol. Chem.*, 1926, 159, 235). It can be seen from our results, that with the hydroquinone substrate, the maximum activity of chow chow peroxidase lies between 4.8 and 5.2 in the acid region, whether the raw or the dialysed sap is used. Wieland and Sutter (*Ber.*, 1928, 61, 1060), proceeding in a different way, find the optimum pH to be 4.6 for the oxygenase of *Lactarius vellereus* (fungus) which

FIG. 6.

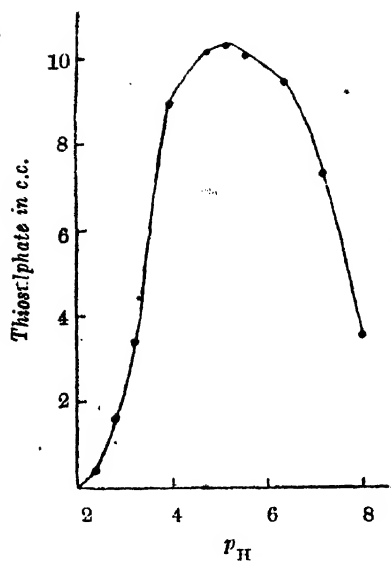


FIG. 7.

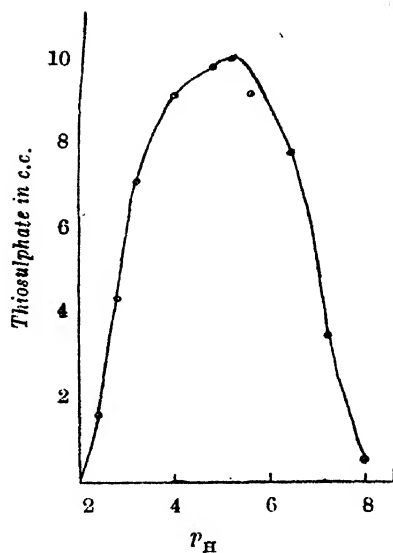
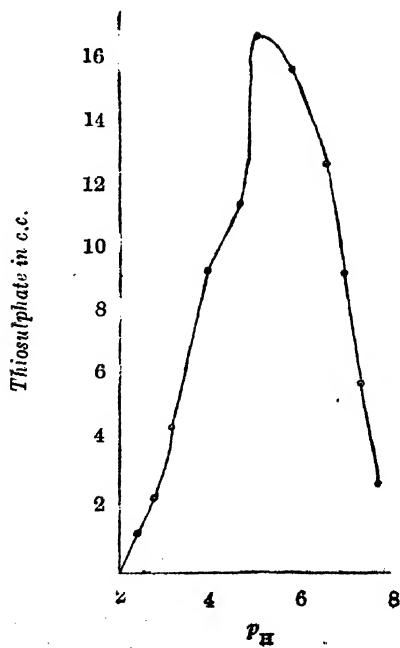


FIG. 8.



autoxidises quinol with the production of hydrogen peroxide. Special precautions had to be taken to prevent the aerial oxidation of hydroquinone solutions which showed signs of oxidation by turning brown even when the pH just exceeded 6.6, and all experiments in the alkaline regions of pH and those approaching alkalinity were therefore carried out with a current of nitrogen bubbling through the liquid. The results are summarised in Tables V, VI and VII, and in Fig. 6, 7 and 8.

Inhibition of the reaction by HCl, and the influence of poisons like KCN and $HgCl_2$, on the activity.—Experiments carried out in normal (pH 0.10), decinormal (pH 1.07) and centinormal (pH 2.02) HCl solutions showed that with dilute solutions of the enzyme the reactivity was practically nil. When, however, the enzyme solution was concentrated, *e. g.*, when the undiluted sap was employed, the action was observed to be fairly rapid even in $N/100$ -HCl. In such cases, the reaction was found to be completely stopped only by the addition of $2N$ -HCl until the final solution had become approximately $N/5$ with respect to it.

The activity of the enzyme is inhibited completely by KCN of $M/10,000$ concentration, while in solutions of $M/100,000$ concentration, the activity is almost unaffected. Mercuric chloride does not seem to have so marked an effect in poisoning the peroxidase; under similar conditions, the peroxidase showed signs of considerable activity even after the addition of a solution of mercuric chloride of $M/1000$ concentration. The results are given in Tables VIII and IX.

Results.

TABLE I. (*cf.* Fig. 1—3).

To 7 c. c. of buffer (pH 5.6) was added 2 c. c. of 1% H_2O_2 , 0.3 g. of hydroquinone, 5 c.c. of sap, and the reaction was stopped by the addition of 2 c.c. of $2N$ -HCl (Total vol., 16 c.c. at 13°).

Time in min.	...	3	5	10	15	20	25	40	60
<i>N/10</i> -Thiosulphate in c.c.									
(1) Undiluted sap	...	18.1	18.1	18.9	18.85	18.85	18.85	18.85	18.85
(2) Sap diluted with its own vol. of water	...	15.65	19.2	19.2	19.2	...	19.2	19.2	19.2
(3) Sap diluted with three times its vol. of water	...	6.6	10.15	15.4	17.7	19.25	19.2	19.1	19.2

When (3) was left over night (16 hours) in the refrigerator, the value obtained was the same, viz., 19.20 c.c. The pH in the above experiments was maintained at 5.6.

At p_H 5.2, 5 c.c. of sap (1:3) gave quinhydrone in a 15 minutes reaction period corresponding to 10.25 c.c. of thiosulphate, while under identical conditions, the same volume of sap (1:7) gave quinhydrone corresponding to 4.62 c.c., showing thereby that the reaction is greatly slowed down by dilution.

TABLE II.

Experiments with varying quantities of enzyme solution (1:3) were made using 5 c.c. of buffer (pH 5.6) and 2 c.c. of 1 per cent. H_2O_2 , 2 c.c. of 2N-HCl being finally added to stop the reaction. In all the experiments the volume of the reaction mixture was 15 c.c. and of wt. hydroquinone, 0.3g.

Vol. of sap (c.c.)	...	1	2	3	4	5	6	10
Vol. of buffer	...	5	5	5	5	5	5	nil
Water (c.c.)	...	5	4	3	2	1	0	1
N/10-Thiosulphate	...	0.35	3.60	6.82	9.60	10.2	10.2	10.1

It is evident that 5 c.c. of the sap, diluted in the above proportion, has the maximum effect under the conditions of experiment given above.

TABLE III (cf. Fig. 4).

Effect of variation in the concentration of H_2O_2 (unbuffered).

H_2O_2 .	Hydroquinone.	Vol. of sap.	2N-Acid to stop reaction.	Water.	N/10-Thio-sulphate.
0.5c.c. (1%)	5 c.c. (4.4%)	5 c.c.	2 c.c.	2.5 c.c.	2.0 c.c.
				2.0	
1.0	"	"	"	2.0	4.60
1.5	"	"	"	1.5	7.40
2.0	"	"	"	1.0	9.70
3.0	"	"	"	0.0	7.40
2.0 c.c. (2%)	5 c.c.	"	"	1.0	5.55
2.5	"	"	"	0.5	8.8
3.0	"	"	"	0.0	3.0
3.5	"	"	1.5	0.0	2.45

The maximum activity is attained with 2 c.c. of H_2O_2 of 1% strength, and rapidly falls off afterwards.

TABLE IV (cf. Fig. 5).

The p_H having been kept constant at 5.2, the activity was measured at different concentrations of hydroquinone, the latter being weighed out each time. The reaction mixture contained 6 c.c. buffer, 5 c.c. sap, 2 c.c. of 1% H_2O_2 , with 2 c.c. 2N-HCl which was finally added to stop the reaction.

Wt. of hydroquinone	...	0.10	0.15	0.2	0.25	0.3	0.35	0.4	0.5	0.6
N/10-Thiosulphate (c.c.)	...	4.10	8.65	9.55	10.0	10.2	10.4	9.85	9.75	8.65

The activity is greatest when the amount of hydroquinone used is 0.35 g. and it can be taken to be almost the same for concentrations of hydroquinone between 0.25 and 0.35 in a total volume of 13 c.c. of the reaction mixture, excluding the volume of HCl added to stop the reaction.

Activity- p_H relationships.—Three sets of experiments were carried out with varying concentrations of hydroquinone for each set of experiments.

TABLE V (cf. Fig. 6).

(1) 6 C.c. buffer, 2 c.c. 1% H_2O_2 , 5 c.c. sap, diluted 4 times, 0.3 g. hydroquinone with the final addition of 2 c.c. 2N-HCl for stopping the reaction.

p_H	...	2.4	2.8	3.2	4.0	4.8	5.2	5.6	6.4	7.2	8.0
N/10-Thiosulphate (c.c.)	...	0.4	1.6	3.4	8.9	10.1	9.85	10.0	9.4	7.3	3.5

TABLE VI (cf. Fig. 7).

(2) 5 C.c. buffer, 5 c.c. H.Q. (0.22 g.), 5 c.c. diluted sap and finally 2 c.c. 2N-HCl.

p_H	...	2.4	2.8	3.2	4.0	4.8	5.2	5.6	6.4	7.2	8.0
N/10-Thiosulphate (c.c.)	...	1.60	4.27	7.0	9.2	9.65	9.85	9.0	7.65	3.4	0.55

TABLE VII (cf Fig. 8).

(3) 7 C.c. buffer, 2 c.c. H_2O_2 , 0.3 g. H.Q. 5 c.c. sap (undiluted and undialysed), and finally 2 c.c. 2N-HCl.

p	...	2.4	2.8	3.2	4.0	4.8	5.2	6.0	6.8	7.2	7.6	8.0
N/10-Thiosulphate (c.c.)		1.30	2.35	4.7	9.7	11.8	17.1	16.05	13.3	9.6	6.05	2.8

Influence of HCN and $HgCl_2$.

TABLE VIII.

(1) See also Table VI for the effect due to variation of p_H).

Conc. of KCN in molarity	...	0.01	0.01	0.001	0.0005	0.00033	0.0001	nil.
p_H	7.24	4.62
N/10-Thiosulphate (c.c.)	...	nil	nil	nil	2.90	5.00	9.8	9.8

TABLE IX.

Conc. of $HgCl_2$.	p_H	N/10-Thiosulphate.	Activity of enzyme alone.
M/100	..	7.85	9.8
M/1000	3.6	9.25	9.8
M/10000	..	9.7	9.8

The Kinetics of the Action of Ammonium Halides on Epichlorhydrin.

SOBHANLAL BANERJEE AND HEMENDRA KUMAR SEN.

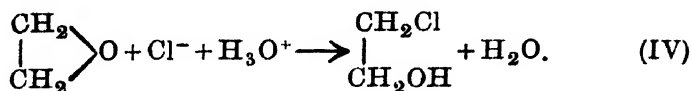
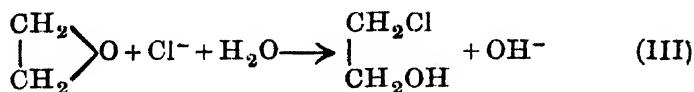
A preliminary note on the action of alkali and ammonium halides on cyclohexene oxide was published by Sen and Barat (*J. Indian Chem. Soc.*, 1927, **4**, 22) and subsequently, the kinetics of the action of epichlorhydrin and ethylene oxide were brought within the scope of investigation (*Proceedings of the Indian Science Congress*, 1927, p. 148). While the work was in progress, Brönsted, Kilpatric and Kilpatric published the kinetics of ethylene oxides (*J. Amer. Chem. Soc.*, 1929, **51**, 428) anticipating to a certain degree our results, although the experimental procedure and the motive were different in the two sets of investigations. Brönsted's object in studying this reaction was to provide a test for his theory of velocity of ionic reactions, according to which the velocity should be given by

$$k = k \cdot C_{\text{Ox}} \cdot C_{\text{H}_3\text{O}^+} \cdot C_{\text{Cl}^-} \cdot f^2$$

where C 's indicate the concentrations of the reacting molecules (the oxide being electrically neutral), and f , the activity coefficient of a univalent ion (*loc. cit.*). There is no doubt that this is a most generalised way of looking at chemical reactions, and the large mass of experimental data brought forward by these authors justify their point of view. We have, on the other hand, approached the interaction of ethylene oxides with salts from the classical orthodox point of view, and have discarded the hitherto believed basic nature of these oxides and have proved that the so-called basicity which was inferred from their power of precipitating oxides of certain metals, is only the result of their combination with the anion and the cation of the acid, the salt of which is brought into reaction. Indeed, the velocity of interaction between these oxides and the salts (haloids), is faster according as there is greater tendency for the formation of the particular halohydrin. Thus, the rates of reaction between chlorides, bromides and iodides with say, epichlorhydrin, are in the order iodide > bromide > chloride. Whilst Brönsted and

Kilpatrics (*loc. cit.*) maintain that 'the addition of acids exhibited by the ethylene oxides, is kinetically only to a minor extent the reason of their apparent basicity', we find, however, that the net result of the action of salt on these oxides, is *the addition of acid*, whatever may be the scheme of reaction. Now, the ability of a substance to add an acid is, by no means, a feature characteristic of bases. 'Bases are characterised by adding protone. Taking up the whole of an acid molecule, is something quite different from the basic function ; it depends upon the anion of the acid in an individual manner and need not have any relation to the strength of the acid added' (Brönsted and Kilpatrics, *loc. cit.*). In fact this is what we also have expressed in our preliminary notes when we have stated that potassium iodide is greater in reactivity than potassium bromide which again is greater in reactivity than potassium chloride with regard to these oxides.

Whether the interaction of acids leading to the addition to the oxides is fundamentally different from the action of their respective salts, is however not yet clear, because the mechanisms in the two reactions may not be the same. Thus, according to Brönsted, the addition of the acid through the salt and the addition of acid *per se* are represented by the two ionic equations :

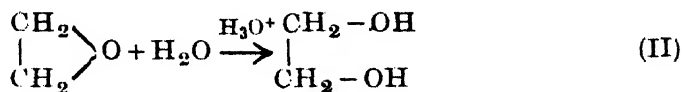


This would evidently, so far as the velocity is concerned, involve according to reaction III, the individual characteristic of the anion, whereas in equation IV, the strength of the H-ion plays the important part. Hence, considered separately, the nature of the salt effect and the acid effect may not be the same. In fact, according to Brönsted although the strongest of all electrically neutral acids *viz.*, perchloric acid, does not react with ethylene oxides in the same way as do the hydro-halogen acids, yet in this group the addition velocity increases with the strength. In the following work, it is the salt effect of the ammonium halides that has been principally investigated. First, because the indicator method of titrating at a constant pH could only be correct for very low

concentrations of salts (in our case moderate to high concentrations have been used), and secondly, because whilst halogen salts of strong bases like potassium and sodium would give rise to strong bases capable of initiating the reverse reaction of reconvertng the hydrins into oxides, ammonia is powerless to do so. In short, stating in Brönsted's terms, our investigations have been restricted to reaction III, with this distinction, however, that it is the three ammonium halides that have been investigated as regards their reactivity with these oxides. The usual method of following the salt effect in our case has been the estimation of ammonia generated with the lapse of time, the indicator used being at first methyl orange but later Wisslow's indicator (mixture of methyl red and methyl blue) and *N*/100-sulphuric acid.

It should be noted here that at such high concentrations of salts e.g., 0.4 mol per litre, the phenomenon of spontaneous glycolisation and that of its acceleration by H ion catalysis though measurable, are not of much consequence, as approximately 90% conversion of the oxide into chlorhydrins, has been reached within a comparatively short period. Ammonia is the measure of the chlorhydrin produced and not of the glycolisation.

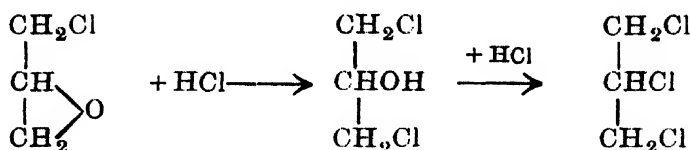
In conformity with the original object of this investigation, the action of yeast on these oxides in a fermenting sugar solution was also investigated, with the result that the presence of reaction II (*loc. cit.*)



i.e., glycolisation was confirmed, yeast being a hydrolytic enzyme. Thus, cyclohexene oxide when allowed to be in contact with a fermenting sugar solution gave cyclohexane-diol in practically quantitative yield, whilst the same with water gave the diol only at elevated temperatures, but that also in small quantities, indicating the comparatively small influence of reaction II in our experiments.

In order to ascertain whether the interaction of epichlorhydrin with ammonium halides is essentially different from the interaction of halogen acids with epichlorhydrin, experiments were performed with various strengths of hydrochloric acid, but in all cases the reaction was incomparably faster than the interaction of the ammonium halide. Thus 0.04*M* epichlorhydrin reacted with 1.2 *M* ammonium chloride to the extent of 85% in 5 hours

whereas hydrochloric acid of similar strength (1.08M) reacted practically to completion in 5 minutes. A distinction however is noticed in the interaction of halogen acids (HCl investigated) with epichlorhydrin, where, with increased concentrations of acid, two molecules of HCl interact in the following way :



The addition of hydrochloric acid of different strengths on epichlorhydrin, was investigated quantitatively, not conductometrically but volumetrically in the following way: A solution of the oxide was mixed rapidly with a hydrochloric acid solution of known volume and known strength. After every 5 minutes or $\frac{1}{2}$ hour as the case may be, a known volume was pipetted off and treated with a weighed quantity of pure precipitated calcium carbonate of which the strength was previously ascertained from the stock bottle. After neutralisation of the remaining acid, the residual calcium carbonate was washed on a filter paper thoroughly, dissolved in a known amount of hydrochloric acid of known strength and the excess determined as usual. The difference between the acid equivalent of the total amount of carbonate taken and this later, gave the amount of hydrochloric acid in excess not added on to the oxide during the period considered. With a little practice, several experiments could be conducted in course of the working hours. This method has a decided advantage over Smith's method of estimating chlorhydrins (by heating with alkali and then titrating the ionically obtained chlorine with silver nitrate) for reason of its very simplicity ; besides, treatment with alkali for several hours in a sealed flask at 70° is also obviated (Smith, Wode, Widhe, *Z. Phys Chem.*, 1927, **130**, 154).

Addition of Hydrochloric Acid to Epichlorhydrin.

To 250 c.c. water 12.15 c.c. of HCl (d 1.19) were added. To 125 c.c of this solution, an alcoholic solution of 0.4625 g. of epichlorhydrin was added and the whole kept at 36° . At intervals of 5 minutes the concentration of the acid was determined in the following way by withdrawing 10 c.c. portions of the reaction mixture.

To 10 c.c. of the reaction mixture, 0.5 g. of CaCO_3 (the acid equivalent of which was previously determined) was added, the excess of the carbonate was then filtered off, washed thoroughly on the filter paper, and dissolved in a known excess of HCl of known strength, and the excess acid determined against $N\text{-Na}_2\text{CO}_3$ solution.

Volumetrically it was found previously that 10 c.c. of the acid solution contained 0.208 g. of HCl, (molarity of the acid = 0.57) 0.5g. of $\text{CaCO}_3 = 9.875$ c.c. of $N\text{-HCl}$

After 5 minutes :

• Residual $\text{CaCO}_3 + 5$ c.c. of $2N\text{-HCl}$ solution = 6.1 c. c of $N\text{-Na}_2\text{CO}_3$; 5 c.c. of $2N\text{-HCl}$ = 10.8 c.c. of $N\text{-Na}_2\text{CO}_3$ solution.

\therefore Residual $\text{CaCO}_3 = 10.8 - 6.1 = 4.7$ c.c. of $N\text{-HCl}$ solution.

\therefore CaCO_3 used up by the acid present in 10 c.c. of the reaction mixture in 5 min. = $9.875 - 4.7 = 5.175$ c.c. of $N\text{-HCl} = 0.1889$ g. of HCl.

Acid originally present in 10 c.c. = 0.208 g.

\therefore Acid used up in 5 minutes by the epichlorhydrin present in 10 c.c. of the reaction mixture = $0.208 - 0.1889 = 0.0191$ g.

\therefore Molarity of the acid used up = 0.052, molarity of epichlorhydrin = 0.04.

\therefore 1 Mol. of epichlorhydrin combines with 1.3 mol. of acid.

After 10 minutes :

Residual $\text{CaCO}_3 + 5$ c.c. of $2N\text{-HCl}$ solution = 6.1 c.c. of $N\text{-Na}_2\text{CO}_3$ solution i.e., no change from the first reading.

After 15 minutes :

No change from the first reading.

Results of similar experiments with different concentrations of hydrochloric acid are given in the following table. The concentration of epichlorhydrin was 0.04 in each

TABLE I.

Conc. HCl.	G. mols. of HCl used up.	No. of mols of HCl combining with 1 mol. of epichlorhydrin.
0.57 M	0.052	1.3
1.08 M	0.08	2.0
1.51 M	0.075	1.875
0.1 M	0.0185	0.385

Calculation of Velocity Constants.

As the temperature coefficients of these reactions were very large, care was taken to ensure the maintenance of the temperature of the thermostat within 0.005° and 0.01° . This was accomplished by electrical relays, and with a little care, it was found quite simple to secure such constancy for hours together without much attention. This was all the more necessary in order to exclude the difference in the values of velocity constants in the same set of experiments as arising from temperature variations. It must be stated in the very beginning that the calculation of the velocity constants presented serious difficulties, as these constants, whichever equation was taken as the basis for calculation, were not satisfactorily concordant. To take as an example, the velocity constants of the interaction between epichlorhydrin and ammonium chloride in molar concentrations of 0.04 and 0.4 respectively when calculated according to monomolecular, a pseudo-monomolecular and a bimolecular equation, gave the following results.

TABLE II.

Time.	N/100- H ₂ SO used up.	$K = \frac{1}{t} \log a/a-x.$		$K = \frac{1}{tb} \log a/a-x.$	$K = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$
		A	B	C	D
1 hr.	2.915	0.0034	0.00125	0.00312	0.00313
2	4.890	0.0030	0.00108	0.0027	0.0030
3	7.019	0.0032	0.00106	3.00265	0.00269
4	8.817	0.0034	0.00103	0.00257	0.00261
5	10.709	0.0034	0.00103	0.00257	0.00263
24	15.797				

In B, C, and D, a stands for the molar concentration of the epichlorhydrin, and in A, a stands for the molar concentration corresponding to the total quantity of the epichlorhydrin actually used up at equilibrium, that is to say, if 0.04 molecule of epichlorhydrin is equivalent to x c.c. of N/100-H₂SO₄, and if at the end of the reaction, the total quantity of epichlorhydrin used up corresponds to y c.c. of sulphuric acid, under the column A, instead of using x c.c. as the active mass, ' y ' the maximum titration value at equilibrium has been used. The use of this value of a has given

the most concordant values of velocity constants, calculated as a pure monomolecular reaction, which however is irreconcilable in view of the fact that the velocity constants vary with the concentration, and hence the reaction could by no means be considered a monomolecular one, but at best could be regarded as pseudo-monomolecular. The means of very closely agreeing constants are given in Table IV. There are, however, reasons to favour the adoption of the maximum titration figure as being the value of the initial active mass, *so far as this particular reaction is concerned*. Firstly, a sort of hydration of the oxide may remove a part of the epichlorhydrin from the sphere of direct reaction with the ammonium salts; secondly, other influences leading to hydration as indicated by reaction II, may be simultaneously acting, and as the rapidity of such hydroxylation in the presence of H ion is great, the active mass of epichlorhydrin actually available for reaction III, is naturally smaller than the initial molar quantity. One notices, however, that all these equations give a certain amount of agreement pointing to the bimolecular nature of the reaction involved, the variations being explained by the side reactions coming into force amongst which the salt effect is the most important.

One can view the whole scheme of reaction from a different point without materially affecting the explanation adduced above. This is based upon the hydrolysis of the ammonium salts in aqueous solution. The minute quantity of halogen acid which is generated thereby, is taken up by the oxide leading to further hydrolysis of the ammonium halide. In this way the concentration of free ammonia increases in the solution depending obviously on the velocity of ammonia liberation and the velocity of the halogen acid addition to the oxide itself. This explains the quicker evolution of ammonia with ammonium bromide and quickest in the case of ammonium iodide. Now, with the increase of ammonium ion in the solution, the hydrolysis of the ammonium halides will naturally be arrested after a time and probably this marks off the stage of equilibrium and maximum titration. With practically no hydrochloric acid in the solution, the conversion of ammonium chloride into ammonia may be regarded as a process of hydrolysis in the presence of a large excess of solvent, water. This way of regarding the scheme of reaction just lends a sort of support to the monomolecular values.

But a most generalised way of looking at the mechanism of the reaction would be not to regard it as arising out of the hydrolysis

of ammonium salts but of the H-ion condition of the solution. Thus a solution of potassium chloride which has an initial p_H 6.4, on treatment with epichlorhydrin, within a few minutes showed a p_H value, 9. In fact, if the p_H value be not allowed to reach the equilibrium value 9, by slowly neutralising the alkali as fast as it is formed, practically the whole of the potassium chloride could be decomposed corresponding to the epichlorhydrin present, and constants agreeing with the true bimolecular equation are obtained (cf. Brönsted, *loc. cit.*). In our titrations, no attempt was made in the beginning to keep the H-ion concentration constant, and hence no really concordant values for the constants fitting with the bimolecular equation could be obtained. The only constancy noticed under our experimental conditions was obtained by substituting our results to the following equation,

$$K = \frac{1}{t} \log \frac{\xi}{\xi - x}$$

where ξ = equilibrium concentration of alkali; $\xi - x$ = the difference between equilibrium concentration and observed concentration of the alkali.

This feature of the reaction has been observed throughout the whole series of experiments (Table III) although no attention was paid to the maintenance of a constant p_H value of the reacting medium, the observance of which gave Brönsted and Kilpatrick's true bimolecular constants. It should be noted, however, that these investigators were working at considerably lower dilutions than in our case. Keeping a constant H-ion concentration in the ammonium halide solutions (these were not investigated by Brönsted), we obtained good bimolecular constants (Tables VI—IX). This would show that whatever may be the salt taken, a true bimolecular reaction takes place only when the p_H value of the particular reacting solution is kept constant. This is not antagonistic to the fact that different anions have different tendencies of addition on epichlorhydrin.

From a perusal of the values of the constants obtained below by using the maximum titration at equilibrium as the active mass of epichlorhydrin with varying molecular concentrations of ammonium halides, it is noticed that over a range of 2–5 (mol. conc. of ammonium halide, when the oxide is one) in the case of ammonium

chloride and bromide (Table IV), there is practically no change in the velocity constant. In the case of ammonium iodide, however, the change in the value of velocity constants is noticeable for every change in its concentration. With higher concentrations of any of these ammonium halides, there is a steady rise and there is irregularity in the value of the constants. But the velocity is considerably increased with the rise in the concentration (Table V). There is thus a positive salt effect. Constant p_a values were maintained by following Brönsted's experimental method (*loc. cit.* p. 441).

TABLE III.

Epichlorhydrin : NH_4Cl = 1 mol : 1 mol. = '04 mol. : '04 Mol.

Time.	N/100- H_2SO_4 used up.	Value of 'K' with 'a' as maximum titration value at equilibrium.
1 hr.	0'409 c. c.	0'000656
2	0'727	0'000669
3	0'999	0'000682
4	1'182	0'000655
5	1'365	0'000668
6	1'59	0'00072
24	3'395	

TABLE IV.

Conc. epichlorhydrin = 0'04M

Temp. = 35°.

Conc. NH_4Cl	...	0'08M	0'12M	0'16M	0'2M
K	...	0'00295	0'0029	0'00284	0'0030
Conc. NH_4Br	...	0'04M	0'08M	0'12M	0'16M
K	...	0'0227	0'0213	0'024	0'025
Conc. NH_4I	...	—	0'08M	0'12M	0'16M
K	0'0442	0'0467	0'0496

TABLE V.

Conc. NH_4Cl	...	0'4M	0'8M	1'2M	2M
K	...	0'0038	0'00492	0'00956	0'00916
Conc. NH_4Br	...	0'4M	—	1'2M	2M
K	...	0'0174	—	0'033	0'0443
Conc. NH_4I	...	0'2M	0'4M	0'8M	—
K	...	0'0688	0'0657	0'1147	0'2714

TABLE VI.

Epichlorhydrin : AmCl = 0.04 mol : 0.04 mol. Temp. 30°. $p_H = 4.6$.

Time in mins.	N/20-Perchloric acid taken up.	$K = \frac{1}{t} - \frac{x}{a(a-x)}$
8	0.091 c.c.	0.000355
13	0.113	0.000271
24	0.181	0.000235
28	0.208	0.000232
32	0.233	0.000227
37	0.261	0.000220
45	0.332	0.000230
49	0.356	0.000227
55	0.392	0.000223
58	0.415	0.000223
63	0.466	0.000231
67	0.482	0.000225
72	0.508	0.000220
77	0.550	0.000229

TABLE VII.

Epichlorhydrin : AmBr = 0.04 mol : 0.04 mol.

Time in mins.	N/10-Perchloric acid used up.	$K = \frac{1}{t} - \frac{x}{a(a-x)}$
11	0.28	0.00159
15	0.418	0.00174
21	0.476	0.00185
26	0.544	0.00130
31	0.640	0.00129
37	0.750	0.00128
40	0.812	0.00127
45	0.880	0.00122
51	1.037	0.00127
55	1.112	0.00126
60	1.170	0.00122
65	1.295	0.00125
70	1.352	0.00121

TABLE VIII.

Epichlorhydrin : AmBr = 0.04 mol : 0.16 mol. Temp. 31°. $p_H = 3.6$.

Time in mins.	N/10-Perchloric acid used up.	$K = \frac{1}{t(a-b)} \times \log \frac{b(a-x)}{a(b-x)}$
6	0.575 c.c.	0.00127
13	1.265	0.00132
18	1.740	0.00128
25	2.306	0.00130
30	2.705	0.00134
36	3.520	0.00133
41	3.740	0.00135
46	4.890	0.00134
53	5.100	0.00137
62	5.580	0.00133
68	6.000	0.00132
72	6.322	0.00138
76	6.625	0.00134
80	6.854	0.00134

TABLE IX.

Epichlorhydrin : AmCl = 0.04 : 0.8 mol.

N/4- Perchloric acid used up.	$K = \frac{1}{t(a-b)} \times \log \frac{b(a-x)}{a(b-x)}$.
14	0.72 c.c. 0.000367
21	1.00 0.000374
25	1.291 0.000363
28	1.410 0.000369
35	1.670 0.000371
39	1.875 0.000365
43	2.000 0.000366
47	2.182 0.000360
53	2.470 0.000365
57	2.645 0.000366
64	2.950 0.000364
68	3.100 0.000360
.72	3.320 0.000361

We gratefully acknowledge our indebtedness to Messrs. Chittaranjan Parat, M.Sc., and Patitpaban Pal, M.Sc., who were associated with the earlier part of this work.

Reviews.

New conceptions in Biochemistry—By Prof. N. R. Dhar.
Published by the Indian Drug House, Allahabad, India, 1932.

In the preface, the author states "The dominant idea in the book is that several diseases are due to lack of a proper and balanced oxidation of the three classes of food materials, the carbohydrates, fats, and proteins. The exaggerated oxidation of one of the three classes of food material in preference to the other two may lead to the incidence of several diseases. The author has ventured to include in the list of metabolism diseases even such ailments as rickets, pillagra, beri-beri, scurvy, special cases of diarrhoea, and cancer." This is a very interesting hypothesis and the author has been able to produce a considerable amount of evidence which is in qualitative agreement with his views. The author has also incorporated in the book a large amount of experimental material obtained in his laboratory on the oxidation of various kinds of food materials in vitro in presence of catalysts and sunlight. It is rather risky to push too far the analogy of chemical processes which take place in vitro into the domain of metabolic processes in living beings, but there is no doubt that such experimental results may give valuable indications of the nature of many mysterious life processes. The book is a very suggestive one and research workers engaged in acquiring new knowledge in this field, would find it well worth careful perusal.

J. C. G.

Studies in Fluorenone. Part II.

BY ANUKUL CHANDRA SIRCAR AND KSHITISH CHANDRA BHATTACHARYYA.

In the first paper in this series published under the caption " Attempts to prepare dyes from fluorenone " (*J. Indian Chem. Soc.*, 1931, 8, 637), a number of fluorenone-2-azomethine, fluorenone-azo, and fluorenonylamide derivatives were described.

The present paper deals mainly with the preparation of bisazo-compounds obtained by diazotising 2:7-diaminofluorenone and coupling the diazo-salt with various phenols and amines, *e. g.*, phenol, resorcinol, salicylic acid, β -naphthol, 2-hydroxy-3-naphthoic acid, 1-naphthylamine-4-sulphonic acid, 1-naphthol-4-sulphonic acid, R-acid (2-naphthol-3:6-disulphonic acid), G-acid (2-naphthol-6:8-disulphonic acid), Cleve's acid (1-naphthylamine-6-sulphonic acid), Laurent's acid (1-naphthylamine-5-sulphonic acid), H-acid (1-hydroxy-8-aminonaphthalene-3:6-disulphonic acid), Schaffer's acid (2-naphthol-6-sulphonic acid), γ -acid (2-amino-8-naphthol-6-sulphonic acid), Chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid) and dimethylaniline.

Of the bisazo derivatives mentioned above, those with phenol, salicylic acid, 2-hydroxy-3-naphthoic acid and dimethylaniline form well defined crystals. The rest were obtained as amorphous or microcrystalline powder. The bisazo dyes are substantive to cotton but a few of them are not absorbed by cotton satisfactorily and even when absorbed the shades are not full. They also dye wool evenly from one per cent. sulphuric acid bath but shades on wool are invariably somewhat lighter than their shades on cotton.

Chanussot (*Anal. Assoc. Quim. Argentina*, 1927, 16, 5) obtained 2-iodofluorenone (m. p. 143-44°) by the oxidation of 2-iodofluorene.

2-Iodofluorenone has now been prepared from 2-aminofluorenone via diazo-reaction.

All attempts to obtain 2:2'-difluorenyl by the action of copper powder (Natur Kupfer C) on 2-iodofluorenone in nitrobenzene or in a sealed tube at temperatures varying from 150° to 350° were unsuccessful. Similar failure to obtain 2:2'-difluorenyl from 2-iodofluorene has been recorded by Korczynski, Karlowaska and Kierzek (*Bull. Soc. chim.*, 1927, 41, 65).

EXPERIMENTAL.

2-Iodofluorenone.—2-Aminofluorenone was diazotised (Diels, *Ber.*, 1901, **34**, 1764) and to this cold diazo solution an excess of potassium iodide solution gradually added with continuous stirring. The mixture was then allowed to remain at the ordinary temperature for about 1 hour and then cautiously warmed until there was no more evolution of nitrogen. The excess of iodine was now removed by sodium thiosulphate and the mixture allowed to stand overnight in a freezing mixture. Next day the separated solid was filtered and repeatedly washed with water. The residue was purified by crystallisation from dilute alcohol. This operation was repeated thrice when finally the iodo compound was obtained as yellow needles, m. p. 144°. (Found: I, 41.8. $C_{13}H_7OI$ requires I, 41.5 per cent.).

Preparation of the fluorenone-2:7-bisazo derivatives.—2:7-Diaminofluorenone (Schmidt, Retzlaff and Haid, *Annalen*, 1912, **390**, 210) was converted into the hydrochloride by warming with excess of concentrated hydrochloric acid. The clear solution was diluted and cooled to about 0°. The amine was tetrazotised in the usual way with the calculated quantity of sodium nitrite. After the diazotisation was complete the solution was quite clear and gave a slight reaction with iodised starch paper. The phenolic or basic constituents were then coupled with the tetrazo-salt in the usual way as with the tetrazo-salt of benzidine. The completion of coupling required from 24 to 41 hours, during which time the mixture was stirred at intervals. The dye stuff was then precipitated by the addition of acid or alkali, washed and purified. None of them melts below 290°. They give characteristic colour reactions with concentrated sulphuric acid, from which water precipitates them unchanged.

The bisazo derivatives obtained are described in the following tables.

Fluorenone-2:7-bisazo Derivatives.

(F = Fluorenone; D = Tetrazo-salt from 2:7-diaminofluorenone).

Name.	Method of preparation.	Appearance and solubilities.	Colour with conc. H_2SO_4 .	Shades of dyeing		Analysis (N).	
				on cotton.	on wool.	Found.	Calc.
F-2:7-bisazo-bis-phenol	D + phenol	Deep brown needles from hot alcohol; moderately soluble in hot alcohol or water, sparingly soluble in hot benzene or acetone.	Deep reddish-violet	Orange yellow	Brownish-yellow	19.66	19.33 p.c.
F-2:7-bisazo-bis-resorcinol	D + resorcinol	Dark brown microcrystalline powder from alcohol; moderately soluble in hot water or alcohol, sparingly soluble in benzene.	Deep violet	Reddish brown	Light reddish brown	12.68	12.98
F-2:7-bisazo-bis-salicylic acid	D + salicylic acid	Deep brown needles from acetic acid; moderately soluble in hot acetic acid, sparingly soluble in alcohol, benzene or water.	Deep reddish violet	Orange yellow	Light brownish-yellow	11.16	11.02
F-2:7-bisazo-bis- β -naphthol	D + β -naphthol	Deep brown crystalline powder; moderately soluble in hot benzene, sparingly soluble in hot alcohol and insoluble in water.	Deep violet	Light shades of violet (practically unabsorbed)	Light violet	10.92	10.76

Fluorenone-2:7-bisazo Derivatives.

Name.	Method of preparation.	Appearance and solubilities.	Colour with conc. H ₂ SO ₄ .	Shades of dyeing		Analysis (N).	
				on cotton.	on wool.	Found.	Calc.
F.2:7-bisazo-bis-2-hydroxy-3-naphthoic acid	D + 2-hydroxy-3-naphthoic acid	Brownish violet rectangular crystals from alcohol; moderately soluble in hot alcohol, acetic acid or water.	Bluish violet	Practically unabsorbed	Violet-brown	9.40	9.20 p.c.
F.2:7-bisazo-bis-1-naphthylamine-4-sulphonic acid	D + 1-naphthylamine-4-sulphonic acid	Red powder from hot alcohol; moderately soluble in hot alcohol, acetone or water.	Blue	No absorption	Light violet-red	12.53	12.39
F.2:7-bisazo-bis-1-naphthol-4-sulphonic acid	D + 1-naphthol-4-sulphonic acid	Deep reddish brown powder from hot alcohol; moderately soluble in hot water, benzene or alcohol.	Deep blue	Light shades of violet (full shades not obtained)	Violet-brown	8.47	8.23
F.2:7-bisazo-bis-2-naphthol-3:6-disulphonic acid	D + R-acid	Reddish violet microcrystalline powder from acetic acid; moderately soluble in hot water or acetic acid and sparingly soluble in alcohol.	Bluish violet	Light shades of violet (full shades not obtained)	Violet-brown	7.04	6.82

Fluorenone-2:7-bisazo Derivatives.

Name.	Method of preparation.	Appearance and solubilities.	Colour with conc. H ₂ SO ₄ .	Shades of dyeing		Analysis (N).	
				on cotton.	on wool.	Found.	Calc.
F:2:7-bisazo-bis-2-naphthol-6:8-disulphonic acid	D + G-acid ↓	Brownish violet from acetic acid; moderately soluble in water or acetic acid and sparingly soluble in alcohol.	Deep red	Light reddish-brown (full shades not obtained)	Reddish-orange	7.07	6.82
F:2:7-bisazo-bis-1-naphthyl-amine-6-sulphonic acid	D + Cleve's acid	Deep brown powder from acetic acid; moderately soluble in acetic acid, sparingly soluble in alcohol or water.	Blue	Very light brown (full shades not obtained)	Brown	12.88	12.79
F:2:7-bisazo-bis-1-naphthyl-amine-5-sulphonic acid	D + Laurent's acid	Deep brown powder from hot alcohol; moderately soluble in hot alcohol or acetone and sparingly soluble in hot water.	Blue	Violet-brown	Reddish-brown	12.87	12.79
F:2:7-bisazo-bis-1-hydroxy-8-aminonaphthalene-3:6-disulphonic acid	D + H-acid	Deep brown amorphous powder; moderately soluble in hot water, sparingly soluble in hot benzene or acetone.	Deep blue	Deep blue	Grey	9.21	9.65

Fluorenone-2:7-bisazo Derivatives.

Name.	Method of preparation.	Appearance and solubilities.	Shades of dyeing		Analysis (N).	
			on cotton.	on wool.	Found.	Calc.
F-2:7-bisazo-bis-2-naphthol-6-sulphonic acid	D + Schaffer's acid	Violet powder from hot alcohol; moderately soluble in hot water, alcohol or benzene and sparingly soluble in acetone.	Violet-brown	Reddish-brown	8.41	8.23
F-2:7-bisazo-bis-2-amino-8-naphthol-6-sulphonic acid	D + γ -acid	Deep brown powder from acetic acid; moderately soluble in water or acetic acid and sparingly soluble in alcohol or acetone.	Bluish violet	Violet-brown	12.08	11.83
F-2:7-bisazo-bis-1:8-dihydroxy-naphthalene-3:6-disulphonic acid	D + Chromotropic acid	Bluish violet amorphous powder; moderately soluble in hot water, acetone or acetic acid and sparingly soluble in alcohol.	Deep greenish blue	Bluish-violet	6.60	6.42
F-2:7-bisazo-bis-dimethylaniline.	D + dimethylaniline	Deep brown needles from acetic acid; moderately soluble in hot alcohol, acetic acid or dilute hydrochloric acid and sparingly soluble in acetone or water.	No absorption	Brown	18.09	17.72

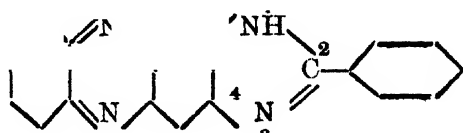
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Studies in Heterocyclic Compounds. Part II.

BY ANUKUL CHANDRA SIRCAR AND INDU BHUSAN PAL.

In the first communication in this series (*J. Indian Chem. Soc.*, 1925, 2, 312) Sircar and De studied the properties of the diheterocyclic compounds obtained from 2:3-diaminophenazine (Ullmann and Mauthner, *Ber.*, 1902, 35, 4302). In all the compounds described the two dissimilar heterocyclic nuclei were separated by a benzene ring, e.g., 4:5-phenazino-2-phenyliminazole.



The present investigation is a continuation of the work of Sircar and De (*loc. cit.*) and was undertaken with the object of studying how in compounds containing two dissimilar adjacent heterocyclic rings in their molecules, the properties of the different heterocyclic nuclei are affected by one another and how the properties of such compounds differ from those of the corresponding compounds in which the two heterocyclic rings are separated by a benzene ring.

$\alpha\beta$ -Diaminoquinoxaline (Bladin, *Ber.*, 1885, 18, 72), which already contains an azine ring was chosen as the starting material. The idea was to prepare diheterocyclic compounds through the two *ortho*-amino groups and to study the properties of the resulting bodies in the manner indicated before.

With this object $\alpha\beta$ -diaminoquinoxaline has been condensed with phthalic, naphthalic, camphoric and diphenic anhydrides and the *o*-benzoylene-, *o*-naphthoylene-, *o*-camphoroylene-, *o*-diphenoylene- $\alpha\beta$ -quinoxalinoiminazoles are obtained.

The quinoxaline has also been condensed in the presence of a solvent with a number of aldehydes and the following iminazoles have been prepared : 4:5-quinoxalino-2-phenyliminazole, 4'-methyl-, 4'-nitro-, 2'-hydroxy-, 3'-nitro-, 2': 4'-dihydroxy-, 4'-methoxy-, -4'-dimethylamino-4:5-quinoxalino-2-phenyliminazoles, and 4:5-quinoxalino-2-furfuryliminazole.

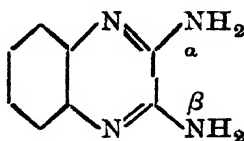
If the condensations are carried out in the absence of any solvent iminazoles of the above type are not formed, but *N*-substituted iminazoles (*cf.* Ladenburg, *Ber.*, 1878, 11, 590, 1648; Hinsberg, 1886, 19, 2025 ; 1887, 20, 1585) are obtained by the condensation of one molecule of the diamine with two molecules of the aldehyde with the liberation of two molecules of water.

The following have been prepared in that way: 4:5-quinoxalino-1-benzyl-2-phenyliminazole, 4:5-quinoxalino-1-*o*-hydroxybenzyl-2-*o*-hydroxyphenyliminazole, and 4:5-quinoxalino-1-*p*-methoxybenzyl-2-*p*-methoxyphenyliminazole.

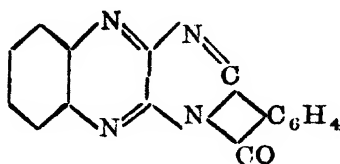
From the study of the properties of the complex heterocyclic compounds described it is found that in them, in most cases, the properties of the corresponding simpler heterocyclic bodies are to some extent modified. For example, the complex iminazoles are much less soluble in the commoner organic solvents than the corresponding simpler iminazoles, obtained from *o*-phenylenediamine. Again from a comparison of the properties of the heterocyclic compounds in which the two hetero-rings are adjacent to one another with those of the corresponding compounds obtained from 2:3-diaminophenazine (Sircar and De, *loc. cit.*), in which the two hetero-rings are separated by a benzene nucleus, it is found that in some of the properties there is a marked difference between the compounds of the two series, *e.g.*, the colours of the compounds of the former type are invariably lighter than those of the compounds of the latter type. A comparative statement of the colours of compounds of the two types is given below.

Names of the compounds.	Colour.
{ <i>o</i> -Benzcylene- $\alpha\beta$ -quinoxalinoiminazole	Very light yellow
{ „ 2:3-phenazinoiminazole	Bright yellow
{ <i>o</i> -Naphthoylene- $\alpha\beta$ -quinoxalinoiminazole	Yellow
{ „ „ -2:3-phenazino- „	Bright yellow
{ <i>o</i> -Camphoroylene- $\alpha\beta$ -quinoxalino- „	Light dirty yellow
{ „ „ 2:3-phenazino- „	Yellow
{ 4:5-Quinoxalino-2-phenyliminazole	Yellow
{ 4:5-Phenazino- „ „	Shining brown red
{ 3'-Nitro-4:5-quinoxalino-2-phenyliminazole	Yellowish white
{ „ „ 4:5-phenazino- „	Orange yellow
{ 4'-Methoxy-4:5-quinoxalino- „	Light orange yellow
{ „ 4:5-phenazino- „	Orange yellow
{ 4'-Dimethylamino-4:5-quinoxalino- „	Brownish yellow
{ „ „ 4:5-phenazino- „	Chocolate red

EXPERIMENTAL.

 $\alpha\beta$ -Diaminoquinoxaline.

It was obtained in the purest form and best yield by adopting the following procedure: To a solution of *o*-phenylenediamine (10 g.) in methyl alcohol (30 c.c.), cyanogen gas, generated by the addition of a concentrated solution of potassium cyanide to a copper sulphate solution and heating, was passed until the deposition of a yellow precipitate of the diaminoquinoxaline was complete. After separation of the precipitate the mother liquor was concentrated and cyanogen gas was again passed through it when a further yield of the yellow precipitate was obtained. The diamine crystallised from pyridine in light yellow rhombic plates, not melting below 300° (cf. Bladin, *loc. cit.*), yield 5 g.

o-Benzoylene- $\alpha\beta$ -quinoxalinoiminazole.

The fused mass, obtained by heating an intimate mixture of $\alpha\beta$ -diaminoquinoxaline (0.5 g.) and phthalic anhydride (0.5 g.) on the oil-bath at $200-20^{\circ}$ for $\frac{1}{2}$ hour, was allowed to cool and powdered. It crystallised from pyridine, on cautious addition of hot water, as very light yellow fibrous needles, m.p. above 300° . It is soluble in alcohol, acetone, chloroform, amyl alcohol, pyridine, nitrobenzene or acetic acid, but insoluble in ether, benzene, dilute acids, or alkalis. It dissolves in strong sulphuric acid giving a red coloration. (Found: N, 20.47. $C_{16}H_8O_2N_4$ requires N, 20.59 per cent.).

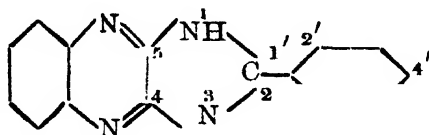
The following three iminazoles were prepared and purified in the same way as and possess properties similar to the preceding compound.

o-Naphthoylene- $\alpha\beta$ -quinoxalinoiminazole, fine long yellow needles. (Found: N, 17.33. $C_{20}H_{10}ON_4$ requires N, 17.39 per cent.).

o-Camphoroylene- $\alpha\beta$ -quinoxalinoiminazole, light dirty yellow needles, m.p. 280° . (Found: N, 18.59. $C_{18}H_{18}ON_4$ requires N, 18.30 per cent.).

o-Diphenoylene $\alpha\beta$ -quinoxalinoiminazole, brownish yellow minute needles. It gives green-yellow fluorescence in chloroform or alcohol solution. (Found: N, 16.24. $C_{22}H_{12}ON_4$ requires N, 16.10 per cent.).

4:5-Quinoxalino-2-phenyliminazole.



A mixture of $\alpha\beta$ -diaminoquinoxaline (0.5 g.), benzaldehyde (1 g.) dissolved in a small quantity of pyridine was heated under reflux for 1 hour. The excess of benzaldehyde was removed by sodium bisulphite and shaking with water. The separated iminazole was washed with dilute hydrochloric acid and water and finally crystallised from acetic acid in beautiful small yellow rectangular needles, m.p. 290° (with previous shrinking at 275°). It is insoluble in dilute hydrochloric acid in the cold but dissolves slowly in the warm acid. It is sparingly soluble in benzene, alcohol or acetone, and readily soluble in nitrobenzene, pyridine or acetic acid. It gives red coloration with strong sulphuric acid. (Found: N, 22.37. $C_{15}H_{10}N_4$ requires N, 22.76 per cent.).

The following iminazoles were prepared, except where otherwise mentioned, in the same way as and possess properties, except where otherwise stated, similar to the preceding compound. In majority of the cases the reaction was complete in $\frac{1}{2}$ hour. When equimolecular quantities of the diamine and the aldehyde were taken, the subsequent treatment with sodium bisulphite solution was not done. The condensation product separated from pyridine solution on dilution with water. They do not melt below 300° .

4'-Methyl-4:5-quinoxalino-2-phenyliminazole, from the diamine (0.5 g.) and *p*-tolylaldehyde (2 g.), separated from acetic acid as light brownish yellow pear-shaped needles. It is soluble in alcohol, pyridine, nitrobenzene, acetic acid, chloroform, or amyl alcohol. (Found: N, 21.14. $C_{16}H_{12}N_4$ requires N, 21.53 per cent.).

4'-Nitro-4:5-quinoxalino-2-phenyliminazole, from equimolecular proportions of the diamine and *p*-nitrobenzaldehyde, crystallised from dilute alcohol in shining red long rectangular plates. (Found: N, 23.78. $C_{15}H_9O_2N_5$ requires N, 24.05 per cent.).

3'-Nitro-4:5-quinoxalino-2-phenyliminazole, separated from alcohol in yellowish white needles. It dissolves in concentrated sulphuric acid with yellow coloration. (Found: N, 24.35. $C_{15}H_9O_2N_5$ requires N, 24.05 per cent.).

2'-Hydroxy-4:5-quinoxalino-2-phenyliminazole, from the diamine (0.5 g.) and salicylic aldehyde (2 g.), crystallised from acetic acid in brown needles. It dissolves in alkali and is also readily soluble in nitrobenzene, pyridine, alcohol or acetone. (Found: N, 21.23. $C_{15}H_{10}ON_4$ requires N, 21.37 per cent.).

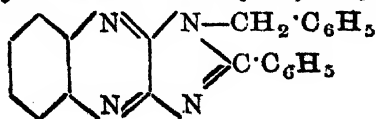
2':4'-Dihydroxy-4:5-quinoxalino-2-phenyliminazole, obtained by the condensation of $\alpha\beta$ -diaminoquinoxaline and resorcylic aldehyde, crystallised from acetic acid in yellow needles. It is soluble in alkali. It dissolves readily in nitrobenzene or amyl alcohol, but less readily in alcohol or acetone. (Found: N, 19.69. $C_{15}H_{10}O_2N_4$ requires N, 20.14 per cent.).

4':Methoxy-4:5-quinoxalino-2-phenyliminazole, from the diamine (0.5 g.) and anisic aldehyde (2 g.), after being separated from the unreacted anisic aldehyde, crystallised from dilute pyridine as light orange-yellow hexagonal prisms. It gives violet yellow fluorescence when its alcoholic or pyridine solution is diluted with water. It is insoluble in chloroform and soluble in nitrobenzene or acetic acid. (Found: N, 20.58. $C_{16}H_{12}ON_4$ requires N, 20.29 per cent.).

4'-Dimethylamino-4:5-quinoxalino-2-phenyliminazole, from dimethyl-*p*-aminobenzaldehyde and the diamine, was obtained as brownish yellow rectangular plates. With strong sulphuric acid it develops a light yellow colour. (Found: N, 23.97. $C_{17}H_{13}N_5$ requires N, 24.22 per cent.).

4:5-Quinoxalino-2-furfuryliminazole, obtained in the usual way from diaminoquinoxaline (0.5 g.) and furfuraldehyde (5 g.), separated from acetic acid in light yellow brown rectangular plates. It exhibits violet yellow fluorescence when its alcoholic or pyridine solution is diluted with water. (Found: N, 23.19. $C_{13}H_8ON_4$ requires N, 23.73 per cent.).

4:5-Quinoxalino-1-benzyl-2-phenyliminazole.



$\alpha\beta$ -Diaminoquinoxaline (0.5 g.) when heated with benzaldehyde (20 c. c.) for $1\frac{1}{2}$ hour, separated on cooling in brilliant yellow long pear-shaped needles, which after being washed with ether were sufficiently pure for further analysis, m. p. above 300° . It is insoluble in ether or benzene and soluble in pyridine, nitrobenzene or amyl alcohol. With strong sulphuric acid it gives a yellow coloration. (Found: N, 16.30. $C_{22}H_{16}N_4$ requires N, 16.16 per cent.).

4:5-Quinoxalino-1-o-hydroxybenzyl-2-phenyliminazole, prepared in the same way as the preceding compound from the diamine (0.5 g.) and salicylic aldehyde (20 c. c.) was obtained as yellow rectangular plates, not melting below 300° . It is insoluble in dilute acids or chloroform but soluble in alkalis, amyl alcohol, acetone, pyridine, nitrobenzene or acetic acid. It dissolves in strong sulphuric acid with a red coloration. (Found: N, 15.77. $C_{22}H_{16}O_2N_4$ requires N, 15.32 per cent.).

4:5-Quinoxalino-1-p-methoxybenzyl-2-p-methoxyphenyliminazole. — $\alpha\beta$ -Diaminoquinoxaline (0.5 g.) and anisic aldehyde (15 c. c.) were heated together for 1 hour. The reaction mixture was then poured in a concentrated solution of sodium bisulphite. The tarry mass obtained solidified on standing. This was filtered, washed and finally crystallised from acetic acid in very light brownish yellow needles, m. p, $243-45^{\circ}$. Except that it is insoluble in alkalis, its other properties are like those of the preceding compound. (Found: N, 14.38. $C_{24}H_{20}O_2N_4$ requires N, 14.14 per cent.)*

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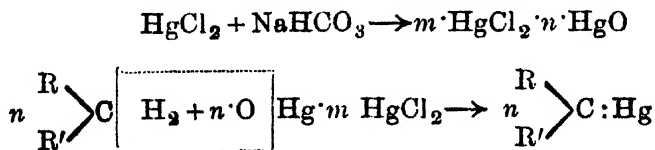
* The work was finished in 1925. Due to certain unforeseen accident the publication has been delayed.

Mercuration of Compounds Containing a Reactive Methylene ($-\text{CH}_2$) Group by means of Mercuric Chloride. Part II.

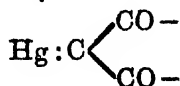
BY K. G. NAIK AND R. P. PATEL.

It is well known that when an aqueous solution of mercuric chloride is boiled with sodium bicarbonate, mercuric oxychlorides are precipitated (Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1923, Vol. IV, p. 833; Millon, *Ann. chim. phys.*, 1846, iii, 18, 372). These oxychlorides differ in their composition according to the experimental conditions and are usually expressed as double compounds of mercuric chloride and mercuric oxide. But it is possible to conceive that when to a boiling aqueous alcoholic solution of mercuric chloride and a reacting organic compound, a solution of sodium bicarbonate is added, the above double compounds of mercury, no sooner are they formed in an incipient condition than, would react with the organic compound present. With such a possibility, the organic compounds containing a reactive methylene group would, under the above conditions, give products containing the grouping $>\text{C}:\text{Hg}$. Such has actually been found to be the case.

The course of reaction may be expressed as :



The following substituted amides of malonic acid and acetoacetic acid when mercured under the above conditions, gave products of the general formula :



(1) Malonmonophenylamide, (2) malonmono-*o*-toluidide, (3) malonmono-*p*-toluidide, (4) malonmono-*m*-toluidide, (5) malonmono-*a*-

naphthylamide, (6) malonmono- β -naphthylamide, (7) malonmono-1:3:4-xylylide, (8) malonamide, (9) ethyl malonate, (10) ethyl acetoacetate, (11) acetoacetanilide, (12) acetoacet-*o*-toluidide, and (13) acetoacet-*p*-toluidide.

That the compounds obtained do not contain admixed mercuric oxychlorides, is shown by the fact that they come out of the mixture as white precipitates which when separated and analysed were found to contain no chlorine; and at no time during the reaction was any change of colour observed. Furthermore, the mercury derivatives were insoluble in the ordinary solvents, whereas the original amides are quite soluble.

The resultant products decompose on treatment with dilute 0.25*N*-hydrochloric acid giving the original amide and mercuric chloride. With hydrogen sulphide they react quantitatively giving black mercuric sulphide. Potassium iodide decomposes the compounds forming the original amide and at the same time liberating two equivalents of alkali for each molecule of the product. Phenylhydrazine and hydrazine hydrate decompose the above compounds with the separation of metallic mercury. The above reactions clearly indicate the existence of a weak C—Hg linkage, which is usually found in compounds, containing mercury attached to a carbon atom in α -position to a carbonyl group.

From considerations such as, (a) the formation of a mercury derivative from ethyl acetoacetate and ethyl malonate, (b) the non-rupture of the C—Hg linkage under conditions which involve the rupture of N—Hg linkage (Ley and Kissel, *Ber.*, 1899, **32**, 1357), (c) the behaviour of the resultant compounds in a way similar to those having mercury attached to a carbon atom in α -position to a carbonyl group (Billman, *Ber.*, 1902, **35**, 2582; Schoeller and Schrauth, *Ber.*, 1908, **41**, 2091; Petterson, *J. pr. Chem.*, 1912, *ii*, **86**, 498; Schrauth and Bauerschmidt, *Ber.*, 1914, **47**, 2740); (d) the quantitative decomposition by potassium iodide, and (e) the formation of dibromomalonamide, with bromine as advanced in a previous communication (Naik and Patel, *J. Indian Chem. Soc.*, 1932, **9**, 185), the above constitution has been assigned to the compounds described herein.

EXPERIMENTAL.

Mercurimalonmonophenylamide, (I).— Malonmonophenylamide (1 g.) and mercuric chloride (1.15 g.) were dissolved in alcohol and

the solution heated to boiling in a flask. To the hot solution was added a solution of sodium bicarbonate (1 g.). The solution became turbid as the compound began to separate and there was effervescence due to the escape of carbon dioxide. The flask was then heated for $\frac{1}{2}$ hour to complete the reaction. The precipitate was then filtered hot at the pump, washed thoroughly with the alcohol and subsequently with distilled water. The product is insoluble in most of the ordinary organic solvents. It melts with decomposition at $275-78^{\circ}$. (Found: N, 7.25; Hg, 53.29. $C_9H_8O_2N_2Hg$ requires N, 7.44; Hg, 53.19 per cent.).

Action of dilute hydrochloric acid on (I).—The compound (I) on treatment with hot 0.25N-HCl went into solution which when concentrated and cooled deposited crystals of malonmonophenylamide, m.p. 164° .

Action of hydrogen sulphide on (I).—The compound (I) (0.6039 g.) was suspended in 30 p. c. alcohol and a slow current of hydrogen sulphide gas was passed into the solution till the precipitation of mercury as mercuric sulphide was complete. The precipitates were then filtered through a Gooch crucible and washed repeatedly with alcohol and water till free from hydrogen sulphide and the amide formed by the decomposition of the compound. It was then washed with carbon disulphide (20 c.c.) and pyridine (20 c.c.) to remove the sulphur which might have been precipitated together with mercuric sulphide. It was finally washed with alcohol and ether to remove the adhering carbon disulphide and pyridine, dried at $105-10^{\circ}$ and weighed (0.3762 g.). (Found: Hg, 53.69. $C_9H_8O_2N_2Hg$ requires Hg, 53.19 per cent.).

This indicates that the decomposition of the substance with hydrogen sulphide was quantitative.

Action of phenylhydrazine and hydrazine hydrate.—The compound (I) was decomposed when it was treated either with phenylhydrazine or with hydrazine hydrate with the separation of grey metallic mercury which settled down.

Action of bromine on mercurimalonamide.—The mercury derivative suspended in water was treated with an aqueous solution of bromine till no more bromine was absorbed. The flask was then heated to boiling and the solution concentrated. On cooling crystalline precipitates of the bromo-derivative and mercuric bromide were obtained. The precipitates were then filtered and washed with alcohol till free from mercuric bromide. The residue when

dried melted at 208-04°. It was identical with the dibromomalonamide obtained by the direct bromination of malonamide (Freund, *Ber.*, 1884, 17, 782).

Mercurimalonmono-o-toluidide, (II).—This was prepared in exactly the same way as the corresponding malonmonophenylamide derivative (I). The product is insoluble in all the ordinary organic solvents and melts with decomposition at 257-59°. (Found: Hg, 51·6. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·3 per cent.).

Action of potassium iodide on (II).—The compound (II) (0·28 g.) suspended in distilled water was treated with an aqueous solution of potassium iodide (1 g.). Potassium hydroxide was gradually liberated. After a day, the liberated potassium hydroxide was titrated against 0·059N-HCl (23·3 c.c.). It was found that no more potassium hydroxide was liberated, even on further heating the mixture, showing that the reaction was complete in the cold.

The liberation of 1·915 equivalents of alkali indicates that the rupture of C-Hg linkage is almost quantitative in the cold.

Compounds similar to the above have been prepared by the interaction of the compounds (3) to (13) with mercuric chloride in presence of sodium bicarbonate under identical conditions. These have been tabulated in the annexed table.

Reaction products of mercuric chloride with substances containing the reactive methylene group.

(M = Mercurimalonmono—)

Name.	Formula.	M.p. (with decomp.)	Found.	Analysis.
M-phenylamide	...	275.78°	Hg, 53.29 N, 7.25	53.19 p.c. 7.44
M-o-toluidide	$C_9H_9O_2N_2Hg$	257.59°	Hg, 51.6	51.3
M-p-toluidide	$C_{10}H_{10}O_2N_2Hg$	278.79°	Hg, 50.8	51.3
M-m-toluidide	$C_{10}H_{10}O_2N_2Hg$	255°	Hg, 50.9	51.3
M-α-naphthylamide	$C_{13}H_{10}O_2N_2Hg$	269°	Hg, 47.4	46.94
M-β-naphthylamide	$C_{13}H_{10}O_2N_2Hg$	270°	Hg, 47.43	46.94
M-(1:3:4)-xylylide	$C_{11}H_{12}O_2N_2Hg$	270°	Hg, 49.2	49.5
Mercurimalonamide	$C_3H_4O_2N_2Hg$	286°	Hg, 66.62	66.66
Mercuriethyl malonate	$C_7H_{10}O_4Hg$	Does not decompose till 300°	Hg, 56.01	55.85
Mercuriethyl acetacetate	$C_6H_8O_2Hg$	Turns brownish black above 270°	Hg, 60.5	60.93
Mercuriacetoacetanilide	$C_{10}H_9O_2NHg$	205°	Hg, 53.66	53.33
Mercuriacetoacet-o-toluidide	$C_{11}H_{11}O_2NHg$	230°	Hg, 51.75	51.4
Mercuriacetoacet-p-toluidide	$C_{11}H_{11}O_2NHg$	243-47°	Hg, 51.3	51.4
			N, 3.95	3.59

The authors take this opportunity to express their gratitude to the Government of His Highness the Maharaja Gaekwar of Baroda, for a grant which defrayed the expenses incurred in the work.

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The Alkaloids of *Rauwolfia Serpentina*, Benth. Part I.

BY SALIMUZZAMAN SIDDIQUI AND RAFAT HUSSAIN SIDDIQUI.

In the course of a general chemical examination of the roots of *Rauwolfia serpentina*, we have already communicated (*J. Indian Chem. Soc.*, 1931, 8, 667), the isolation of five new alkaloids and characterised them in some detail. We were engaged since in the study of the three main alkaloids, chiefly *ajmaline*, but owing to lack of sufficient substance we could not so far get to decisive conclusions about their constitution. As however, a recent publication of Van Itallie and Steenhauer (*Arch. Pharm.*, 1932, 270, 313) on the subject has brought up some points of controversy, we feel constrained to publish the results already obtained and discuss them in the light of that publication.

The Dutch authors have been able to isolate only three alkaloids from the root of *R. S.*, which seem to correspond to *ajmaline*, *ajmalinine* and *serpentinine*. Their alkaloids B and C melt three degrees lower than *serpentinine* and *ajmalinine* respectively and the rotation of the alkaloid C ($[\alpha]_D = -76.4^\circ$) is -20.6° less than that of *ajmalinine* ($[\alpha]_D = -97^\circ$), due probably to its contamination with the strongly positive *ajmaline*. Their failure to get *serpentine* and *ajmalicine* is easily accounted for by their using ammonia and ether as a means of extraction. *Serpentine* is not liberated by ammonia and both *serpentine* and *ajmalicine* are almost insoluble in ether. The authors have given *ajmaline* another name "*Rauwolfine*," on the basis of a formula, higher than that given by us for *ajmaline* by one carbon atom, in the face of almost identical colour reactions, optical activity and melting points: *Ajmaline*, m.p. $158^\circ-60^\circ$, $[\alpha]_D^{33} = +128^\circ$ (in 1 % CHCl_3 solution). *Rauwolfine*, m.p. about 160° , $[\alpha]_D = +131.1^\circ$ (in 1 % CHCl_3 solution).

The slightly lower rotation of *ajmaline* is easily explained by the fact that *ajmaline* containing $3\frac{1}{2}$ molecules of water of crystallisation, i.e., 17.0% of active matter, was used by us for the determination

of optical activity, whereas the base used by the Dutch authors contained 1 CH_3OH of crystallisation, i.e., only 8.7% of optically inactive matter.

The reason for the disparity in the formulae of ajmaline and rauwolfine lies in the fact, that we had assigned the formula $\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2$ to ajmaline on the basis of dehydration at 100° in *vacuo* while the Dutch authors combusted their base after heating it to constant weight at 150° to remove the methyl alcohol of crystallisation. As later observations showed, ajmaline does tenaciously retain $\frac{1}{2}$ a molecule of water more, after losing three molecules of water at 100° , which it gives up only on heating upto about 150° . This view is further supported by the fact that ajmaline* shows the presence of 2 active H after heating to constant weight at 100° and only 1 active H after complete dehydration at 150° . In the light of these observations the original formula of ajmaline $\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2$ resolves itself into $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$, $\frac{1}{2}\text{H}_2\text{O}$. [Found: (*loc. cit.* p. 673) C, 73.0; H, 8.12; N, 8.8. $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$, $\frac{1}{2}\text{H}_2\text{O}$ requires C, 72.6; H, 7.8; N, 8.1 per cent. $\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2$, requires C, 73.6; H, 8.0; N, 8.6 per cent.]. The platinum value of the chloroplatinate as given by us in the last communication (*loc. cit.*) though within the limits of error for the C_{20} formula agrees even more closely with the C_{21} formula. [Found: Pt, 17.9. ($\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$, HCl)₂, PtCl_4 requires Pt, 18.0 per cent. ($\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2$, HCl)₂, PtCl_4 requires Pt, 18.4 per cent.]. The nitrogen value is a little too high for the C_{21} formula, but in the nature of the case the C and Pt values have to be given greater weight in deciding between the two formulae, differing by one carbon atom.

But while all the general characteristics of the base rauwolfine point to its identity with ajmaline we have to postpone a definite conclusion to this effect as the Dutch authors have made no mention of the presence of an active H in rauwolfine in the course of its group analysis and have, moreover, showed after the method of Herzig and Meyer the absence of N-CH_3 in the base, whereas we believe to have established the presence of an N-CH_3 and an active H in ajmaline, and showed the likelihood of ajmaline containing the group $:\text{NHCH}_3$ in its molecule.

The secondary character of ajmaline we concluded from its yielding a non-basic crystalline nitroso derivative and a non-basic crystalline monobenzoate. A crystalline acetyl derivative could not be formed but we succeeded in getting a crystalline methyl derivative

of ajmaline out of a crystalline methiodide, which showed the presence of two N-CH_3 groups whereas ajmaline itself was found to contain only one N-CH_3 . As one of the two N atoms in ajmaline is non-basic, it appears that the methyl groups and the imino-hydrogen are both linked to one and the same nitrogen and the formula of ajmaline might be further represented as $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}(\text{NHCH}_3)$.

Ajmaline does not contain either a hydroxy or methoxy group and we have not been able so far to account for the two oxygen atoms contained in its molecule. On being heated upto about 200° ajmaline was changed into a brittle varnish-like reddish mass, out of which we could isolate a crystalline base melting at 256° , which we have provisionally called "pyroajmaline".

Serpentine, serpentinine, and ajmalicine also form nitroso derivatives and appear to be secondary bases. Considering the fact, that number of secondary bases in nature is very limited, their prevalence particularly in the roots of a plant is rather striking but as our investigation on the bark of *Holarrhena antidysenterica* (this volume) have brought to light a series of apparently secondary bases, the *Apocynaceae* family to which the two plants belong might be considered as particularly rich in secondary bases.

In the light of our observations in case of ajmaline the empirical formulae of ajmalinine and serpentine were also revised, but owing to the lack of sufficient amount of substance no decisive results could be so far obtained. It may, however, be noted here, that serpentine also appears to retain some more water of crystallisation after heating to constant weight at 150° , while ajmalicine does not. Neither of these bases were found to contain an N-CH_3 group, but each of them showed the presence of one OCH_3 group.

A further point of interest has been brought up through the isolation of 3 new bases from an African species of *Rauwolfia*, *Rauwolfia caffra*, by Koepfli (*J. Amer. Chem. Soc.*, 1931, **54**, 2412). The chief alkaloid has been named rauwolfine ($\text{C}_{20}\text{H}_{26}\text{O}_3\text{N}_2$, d. p. $235-38^\circ$) and appears to be a quarternary base. Though the two plants are so allied, the base from *R. caffra* appear to be very different from those of *R. serpentina*.

EXPERIMENTAL.

Determination of active H in ajmaline (Zerewitinoff's method).—After complete dehydration at 150° [Found: H, 0.23.

$C_{21}H_{26}O_2N_2$ requires (for 1 active H) H, 0.29 per cent.]. After heating to constant weight at 100° in *vacuo* [Found: H, 0.59. $C_{21}H_{26}O_2N_2$, $\frac{1}{2}H_2O$ requires (for 2 H) H, 0.59 per cent.].

Determination of N-CH₃ in ajmaline (Herzig and Meyer's method) ajmaline showed the presence of 1N-CH₃. [Found: CH₃, 5.06. $C_{21}H_{26}O_2N_2$ requires (for 1N-CH₃) CH₃, 4.43 per cent.].

Nitrosoajmaline.—To a cooled solution of ajmaline (1 mol., 0.33 g.) in 10 p. c. acetic acid, a well cooled solution of sodium nitrite (1.5 mol., 0.12 g.) was slowly added. A cream yellow granular precipitate was produced, which was filtered after keeping the reaction mixture well corked at room temperature overnight and well washed first with warm 5 p. c. acetic acid, then with water, to remove the unchanged base. On recrystallising from dilute alcohol nitrosoajmaline formed pale yellow needles, m. p. 209° . [Found: (after drying to constant weight at 100° in *vacuo*) C, 67.7; H, 7.11. $C_{21}H_{25}O_3N_3$ requires C, 68.67; H, 6.81 per cent. $C_{21}H_{25}O_3N_3$, $\frac{1}{2}H_2O$ requires C, 67.02; H, 6.91 per cent.].

Benzoylajmaline.—To a solution of ajmaline (0.5 g.) in pyridine (4 c. c.) was added benzoyl chloride (0.75 c. c.) under good cooling. The thick oil which settled down overnight was washed with dilute acetic acid and taken up with alcohol and water. On cooling the solution, long, white, broad needles (0.3 g.) were obtained, which softened at 134° and melted at 180° . On recrystallisation from benzene after washing it with dilute acetic acid the benzoate began to darken from 140° onwards and melted at $214-16^\circ$. (Found: C, 74.6; H, 8.05. $C_{21}H_{25}O_2N_2 \cdot COC_6H_5$ requires C, 76.02; H, 6.79 per cent.). Evidently this product was not pure enough to give a correct analysis but its distinctly non-basic character confirmed the presence of an imino H in ajmaline.

Methylajmaline.—To a solution of ajmaline (1 mol., 1 g.) in chloroform (3 c. c.) methyl iodide (1.5 mol., 0.7 g.) was added and the mixture left well corked at the room temperature (40°). After 2 days the separated crystalline product was filtered, washed with chloroform and dried (yield 0.95 p. c.). Methylajmaline hydroiodide thus obtained melted at $230-31^\circ$. Its N-CH₃ estimation showed the presence of two N-CH₃ groups. [Found: CH₃, 6.2. $C_{22}H_{28}O_2N_2 \cdot HI$ requires (for 2 NCH₃) CH₃, 6.3 per cent.]. The chloroform solution on evaporation gave a residue (0.27 g.), which melted between $230-50^\circ$, but the amount being too small could not be investigated further.

The crystalline hydriodide was dissolved in acetic acid and the base precipitated from the solution with concentrated NaOH solution, because methylajmaline could not be precipitated by ammonia, and thus, rather contrary to expectations, appears to be stronger than the secondary base, ajmaline. The precipitate was shaken with chloroform, the chloroform solution dried over sodium sulphate and the clear pale yellow residue left on removing the solvent crystallised from moist ethyl acetate in star shaped clusters of needles, m.p. 130° - 31° (softening at 127°). It is easily soluble in alcohol, less so in ethyl acetate, difficultly soluble in ether, insoluble in petroleum ether. It gives the same colour reactions as ajmaline. (Found: C, 74.90; H, 8.85. $C_{22}H_{28}O_2N_2$ requires C, 75.0; H, 7.95 per cent.).

The salts of methylajmaline were prepared in the same manner as in case of ajmaline.

Methylajmaline hydrochloride forms a white powder,* soluble in alcohol but difficultly so in cold water. It softens at 125° , froths up at 132 - 34° (giving off water of crystallisation) and melts at 272° .

Methylajmaline picrate forms a bright yellow powder, which is easily soluble in alcohol but difficultly so in cold water. It begins to froth at 176° and melts at 186° .

Methylajmaline chloroplatinate is an amber coloured powder, soluble in alcohol but insoluble in water. It shrinks with darkening at 203° and melts at 215 - 20° (decomp.).

Effect of heat on ajmaline: pyroajmaline.—On dehydration at 100° in *vacuo* ajmaline melts indefinitely from 160 - 70° . On heating to constant weight at 150° it further loses 2.3 p. c. of water ($C_{21}H_{26}O_2N_2$, $\frac{1}{2}H_2O$ requires H_2O , 2.88 p. c.) and begins to soften at 170° sticking slowly to the sides of the m. p. tube by 185° , the sticky mass melting down at about 256° . On heating ajmaline at 200° for about $\frac{1}{2}$ hour a brittle reddish brown mass is produced which crystallises partly out of moist ethyl acetate in slender needles, m. p. 256° (shrinking at 240°). They lose 6.9 p.c. water of crystallisation when heated to constant weight at 150° (showing $1\frac{1}{2}$ mol of water of crystallisation, if the molecule of pyro-ajmaline should be the same, as that of ajmaline). It is difficultly soluble in chloroform.

Pyroajmaline hydrochloride.—The hydrochloride, prepared by adding ethereal hydrochloric acid in a chloroform-ether solution of the base is an amorphous powder which darkens at 226° , softens at 230° and melts at 238 - 40° (decomp.). It is easily soluble in alcohol and water.

Determination of OCH_3 in ajmalinine (Zeisel's method) showed the presence of one OCH_3 group. (Found: OCH_3 , 8.8. $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}$ requires OCH_3 , 8.96 per cent.).

Determination of OCH_3 in serpentine showed the presence of one OCH_3 group. (Found: OCH_3 , 9.27. $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$ requires OCH_3 , 8.78 per cent.).

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The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part I. The Bromination of Diphenyl- ψ -thiohydantoin and its *ortho*-Tolyl Homologue.

By MOHAMMAD OMAR FAROOQ AND ROBERT FERGUS HUNTER.

It has been shown that treatment of a solution of benzthiazole in chloroform at low temperatures with a molecular proportion of bromine gives rise to a dibromide (Hunter, *J. Chem. Soc.*, 1930, 125), whose properties suggest that the bromine atoms are held to the nuclear nitrogen atom by means of semipolar single bonds, after the manner of attachment of the labile chlorine atoms to the phosphorus atom in phosphorus pentachloride (Prideaux, *Chem. Ind.*, 1923, 42, 672; Ingold and Ingold, *J. Chem. Soc.*, 1926, 1315; Sugden, *J. Chem. Soc.*, 1927, 1176). A similar series of dibromo-addition compounds have also been obtained from the 5-chloro-3-bromo-1-alkylaminobenzthiazoles (Dyson, Hunter, Jones, and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147), which are characterised by their extraordinary thermal stability to temperatures within 20° or so of their melting points, at which rapid decomposition sets in without any indication of an equilibrium of the type which has been observed by Ephraim in the case of alkali perhalides (*Ber.*, 1917, 50, 1069). In the presence of a large excess of the halogen, however, benzthiazole yields a highly unstable tetrabromide, analogous to the more stable tetrabromide of 1-phenylbenzthiazole (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, 44, 826; Hunter, *loc. cit.*). The formation of these compounds by a repetition of the process of singlet

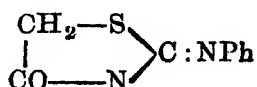
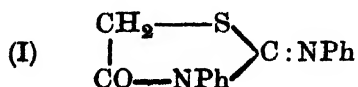
sharing, leading to the production of the $\equiv \text{N} \cdot \overset{\text{Br}}{\underset{\text{Br}}{\text{Br}}}$ complex is not difficult to visualise.

Now it is clear that if this interpretation of the mechanism of formation of these compounds is correct, the phenomenon must permeate, in greater or lesser degree, the whole field of heterocyclic compounds in which hetero atoms containing lone pairs of unshared electrons are encountered. It is therefore the object of this series of investigations, to study the behaviour of different heterocyclic systems towards bromine, and to examine the effect of substituents on the formation and stability of their bromo-addition compounds in relation to their suggested electronic constitution.

Particular interest attaches itself to the compounds of sulphur and nitrogen in view of the apparent expansion of the valency group of sulphur to twelve electrons in sulphur hexafluoride, and it has already been shown that the nuclear sulphur atom of the benzthiazole system exhibits the characteristic inertness of that in thiophen (Hunter, *loc. cit.*). This has been interpreted on the basis of the sextuple group theory of aromatic stability (Armit and Robinson, *J. Chem. Soc.*, 1925, 127, 1605; Goss and Ingold, *J. Chem. Soc.*, 1928, 1268), which receives further support from Hückel's recent wave mechanical analysis of the benzene molecule (*Z. Physik*, 1931, 70, 204). This author has had to make a number of assumptions which may or may not be entirely justifiable, but he has shown that by working out the quantum states of the six electrons over and above those required for joining carbon to carbon and carbon to hydrogen, and applying Pauli's principle, that a system of six electrons constitutes a "closed group" somewhat analogous to the closed groups of the Periodic system. Although the effect of disturbed symmetry in heterocyclic compounds such as pyridine, thiophen, and thiazole which exhibit aromatic characteristics cannot be calculated, it is clearly reasonable to assume that the importance of the sextuple group still persists in relation to their chemical behaviour.

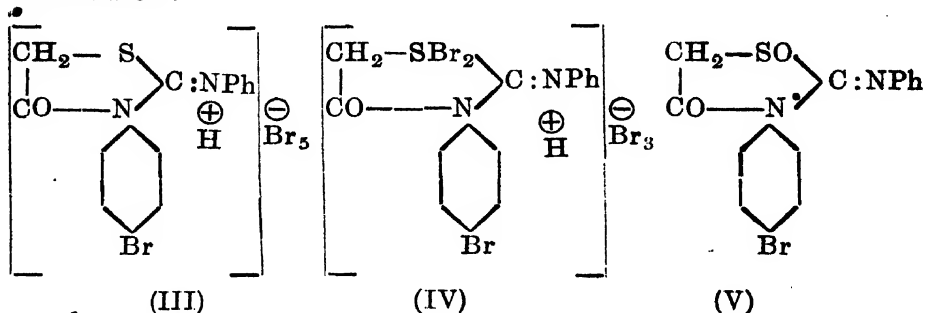
It therefore appeared of interest to examine the reactivity of the reduced thiazole nucleus towards bromine, and the ψ -thiohydantoins were selected for this purpose.

The bromination of diphenyl- ψ -thiohydantoin (I), in chloroform at low temperatures, gave rise to a well defined vermilion compound, possessing the composition of a hexabromide of the tetrahydrothiazole. Only two thirds of its total bromine was, however, labile towards potassium iodide and on reduction with sulphurous acid it yielded 2-phenyl-3-*p*-bromophenyl-4-ketotetrahydrothiazole (II), whose constitution follows from its synthesis from *p*-bromo-*s*-diphenylthiocarbamide and monochloroacetic acid (Dains, Irvin, and Harrel, *J. Amer. Chem. Soc.*, 1921, 43, 613).



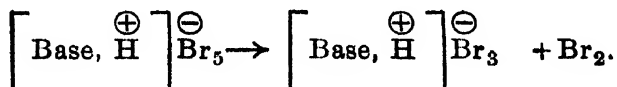
These reactions clearly exclude the possibility of addition of bromine to the double bond of the 2-phenylimino grouping in the original ψ -thiohydantoin, and the bromo-addition compound is evidently a *hydropentabromide* of the bromophenyltetrahydrothiazole (II), which is confirmed by its synthesis from the bromophenyltetrahydrothiazole, hydrogen bromide, and bromine.

There is clearly a choice of formulae (III) and (IV) for the hydropentabromide, depending on whether the sulphur atom of the ψ -thiohydantoin complex is reactive as in the dialkyl sulphides (Cahours, *Annalen*, 1865, 135, 355), or inert as in thiophen and benzthiazole.



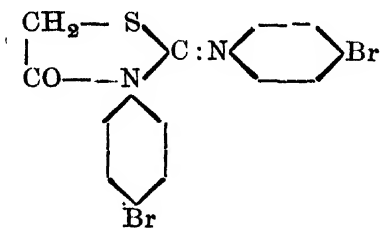
The sulphonium bromide formula (IV) is, however, excluded by the fact that the hydropentabromide yields 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole, and *not* the sulfoxide (V) on treatment with precipitated mercuric oxide.

On exposure to the atmosphere, or on keeping in a desiccator over potassium hydroxide, the hydropentabromide lost bromine yielding a stable yellow *hydrotribromide* of 2-phenyl-3-*p*-bromophenyl-4-ketotetrahydrothiazole. This compound was also obtained by thermal decomposition of the hydropentabromide, under reduced pressure at a temperature some 25° below its melting point, when dissociation took place in accordance with the equation:

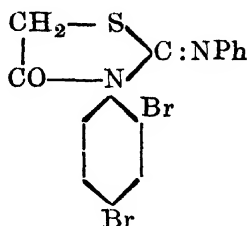


The bromination of 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole in chloroform at low temperatures, yielded an unstable *octabromide*, which regenerated the original ψ -thiohydantoin (II) on treatment with sulphurous acid. On the other hand, its labile bromine content as determined by iodometric titration in chloroform, indicated the presence of only six labile bromine atoms,

It has been shown that this loss is due to nuclear substitution under the conditions of the reaction, leading to the production of a dibromo substitution derivative of diphenyl- ψ -thiohydantoin, which is different from 2-*p*-bromophenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole (VI) which was synthesised from *s*-di-*p*-bromophenylthiocarbamide and monochloroacetic acid (Dains, Irvin, and Harrel, *loc. cit.*), and which is evidently the 2-phenylimino-3-*o*-*p*-dibromophenyl derivative (VII).

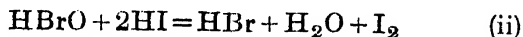
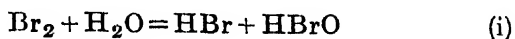


(VI)



(VII)

This difference in reactivity of labile bromine towards sulphurous acid and potassium iodide has already been observed in the case of the tetrabromide of 1-phenylbenzthiazole (Hunter, *J. Chem. Soc.*, 1930, 138), and is evidently due to the fact that the second reaction is preceded by a hydrolysis of labile bromine to hypobromous acid, which then reacts with hydriodic acid in the usual way.



This receives confirmation from the fact that a solution of the octabromide in chloroform undergoes nuclear substitution with the production of the dibromo derivative, on being shaken with water.

The octabromide also regenerated the original 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole on treatment with mercuric oxide, indicating that the perbromide complexes are attached to nitrogen, and that in the ψ -thiohydantoin base as well as in the ammonium ion derived from it, the nuclear sulphur atom retains the characteristic inertness of the sulphur atom in thiazole and benzthiazole. This is of particular interest, since in this case there can be no question of the lone electrons of the sulphur atom being required for the formation of a sextuple group.

The bromination of di-*o*-tolyl- ψ -thiohydantoin (I, with *o*-C₇H₇ in place of Ph) at low temperatures, yielded an unstable *hydroheptabromide* of a monobromo-substitution derivative, which is almost certainly 2-*o*-tolylimino-3-*p*-bromo-*o*-tolyl-4-ketotetrahydrothiazole, although it has not yet been possible to isolate a synthetic specimen of this ψ -thiohydantoin from the condensation of *s*-*o*-tolyl-*p*-bromo-*o*-tolylthiocarbamide and monochloroacetic acid. On exposure to air, the *hydroheptabromide* lost bromine yielding a stable yellow *hydrotribromide*, similar to the compound obtained by degradation of the *hydropentabromide* of 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole.

EXPERIMENTAL.

2-Phenylimino-3-phenyl-4-ketotetrahydrothiazole (diphenyl- ψ -thiohydantoin) was prepared in 90 p.c. yield by heating a solution of thiocarbanilide (23 g.), monochloroacetic acid (9.5 g.) and pyridine (16 c.c.) in alcohol under reflux for 5-6 hours. It separated from alcoholethyl acetate in needles, m. p. 175° (compare Lange, *Ber.*, 1879, 12, 596; Liebermann, *Annalen*, 1881, 207, 123).

2-Phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole *hydropentabromide*. (i) *Bromination of diphenyl- ψ -thiohydantoin*.—A solution of the hydantoin (1 g.) in chloroform (10 c. c.) was cooled to 0–3° and treated with bromine (0.8 c. c. in 0.8 c. c. of the same solvent), when the *hydropentabromide* crystallised after a minute or two. After being dried on porous earthenware, in a vacuum over potassium hydroxide for a short time, it formed glistening vermilion plates which become yellow with loss of bromine vapour at about 140° and had m. p. 161–63° (decomp. with effervescence). [Found: Br (total), 64.1, 64.0; Br (labile), 42.0, 41.6. C₁₅H₁₁ON₂BrS, HBr (Br₄) requires Br (total), 64.2; Br (labile), 42.8 per cent.]. On exposure to air for 24 hours, the *hydropentabromide* lost bromine yielding a stable yellow *hydrotribromide*, which after being digested for a few minutes with boiling chloroform in which it is almost insoluble, and drying in a vacuum, had m. p. 145–46° (decomp.). [Found: Br, 54.0. C₁₅H₁₁ON₂BrS, HBr (Br₂) requires Br, 54.4 per cent.]. On treatment with sulphurous acid and sulphur dioxide, both of these bromo-addition compounds yielded 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole, which separated from ethyl acetate in needles, m. p. 175°. [Found: Br, 23.2; S, 9.3. Calc.: Br, 23.1; S, 9.2 per cent.]. This bromophenyltetrahydrothiazole was also prepared by heating

a mixture of *s*-phenyl-*p*-bromophenylthiocarbamide (6.5 g.), monochloroacetic acid (2 g.) and pyridine (2 c. c.) in alcohol for 3 hours. A mixture of both specimens melted at 175°, but admixture with diphenyl- ψ -thiohydantoin (m. p. 175°) caused a depression of 20 to 25°.

(ii) *Synthesis from 2-phenylimino-3-p-bromophenyl-4-ketotetrahydrothiazole*.—Bromine (1.4 c. c.) was added to a solution of 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole (0.7 g.) and hydrogen bromide (0.3 g.) in glacial acetic acid (5 c. c.), when the hydropentabromide crystallised in shining red plates, m. p. 159-60° (decomp. after losing bromine at 145°) after being rapidly dried on porous earthenware in a vacuum [Found: Br (total), 64.1; Br (labile), 42.8 per cent.]. Curiously enough, this specimen of the hydropentabromide appeared to be more stable to the atmosphere than the specimens prepared by direct bromination (compare Hunter, *loc. cit.*).

(iii) *The action of mercuric oxide*.—Precipitated mercuric oxide, dried at 110°, was added with shaking to a solution of the hydropentabromide in chloroform until decolorisation appeared to be complete. The filtered solution was evaporated and the product was recrystallised from alcohol (animal charcoal) when 2-phenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole was obtained and identified by m. p. and mixed m. p. determination.

(iv) *Thermal dissociation*.—5 g. of freshly prepared hydropentabromide were placed in a dry flask, fitted with a stop-cock, and in series with a soda lime tower, manometer, and an oil pump. The flask was exhausted to 24 mm., placed in an oil-bath at 135-37° and heated for 6 minutes when bromine was copiously evolved with the production of a yellow granular residue consisting of the stable hydrotribromide, which was identified by its properties and also by analysis (Found: Br, 53.8 per cent.).

2-Phenylimino-3-p-bromophenyl-4-ketotetrahydrothiazole octabromide.—A solution of the *p*-bromophenyltetrahydrothiazole (0.5 g.) in chloroform (3 c. c.) was cooled to 0° and treated with bromine (0.7 c. c. in 0.5 c. c. of chloroform) when the octabromide crystallised in glistening red plates, which were dried on porous earthenware in *vacuo* for 5 minutes and immediately analysed with the precautions used for highly unstable compounds of this type (Dyson, Hunter and Soyoka, *J. Chem. Soc.*, 1929, 460), m. p. 161-62°. [Found: Br (total), 72.8; Br (labile), 45.2. $C_{15}H_{11}ON_2Br_8$ requires Br (total),

72.9 ; Br (labile), 62.5 per cent.]. This compound was also obtained by treating a solution of the bromophenyl derivative (0.5 g.) in chloroform (6 c. c.) with bromine (0.6 c. c. in 0.6 c. c. of chloroform). On reduction with sulphurous acid, or on shaking a chloroform solution of the bromide with mercuric oxide the original *p*-bromophenyltetrahydrothiazole was obtained unaccompanied by other products.

Titration and hydrolysis experiments.—(i) A solution of the octabromide in chloroform (50 c. c.) was treated with excess of aqueous potassium iodide and the mixture was decolorised with sodium thiosulphate solution and the chloroform layer was separated, well washed with distilled water, and evaporated on a water-bath. On recrystallisation from alcohol, 2-phenylimino-3-*o*-*p*-dibromophenyl-4-ketotetrahydrothiazole was obtained, m.p. 119–20°, which melted at 120° when mixed with the specimen obtained by hydrolysis of the octabromide. (ii) A solution of the octabromide in chloroform (50 c.c.) was shaken with water (20 c.c.) at intervals during a period of 5 minutes and the mixture was thereafter treated with excess of sulphur dioxide. Evaporation of the chloroform layer yielded the dibromo derivative which separated from alcohol in small needles, m.p. 121°. (Found: Br, 37.2. $C_{15}H_{10}ON_2Br_2S$ requires Br, 37.5 per cent.).

2-*o*-Tolylimino-3-*p*(?)-bromo-*o*-tolyl-4-ketotetrahydrothiazole hydroheptabromide.—A solution of di-*o*-tolyl- ψ -thiohydantoin (0.5 g.) (Pozzi Escot, *Compt. rend.*, 1904, 139, 1032) in chloroform (5 c.c.) was treated with bromine (0.7 c.c.), when the hydroheptabromide crystallised after a short time. The bromo-addition compound formed unstable red glistening needles which were collected on a porous earthenware, rapidly dried in high vacuum, and immediately analysed, m.p. 120–21° (decomp.). [Found: Br (total), 69.3; Br (labile), 49.7. $C_{17}H_{16}ON_2Br_7S$, $HBr(Br_6)$ requires Br (total), 68.4; Br (labile), 51.3 per cent.]. This experiment is typical of a number, and the appreciably high figure for total bromine is due to the same difficulty as that encountered in dealing with other unstable high perbromides of this type which are too unstable to permit crushing of the crystals and redrying in *vacuo* for removal of the last traces of occluded halogen (compare Dyson, Hunter, and Soyka, *loc. cit.*; Hunter, *J. Chem. Soc.*, 1930, 139). Experiments which have been made in this connection on stable hydrotribromides, such as those of 5:4'-dichloro-1-anilinobenzthiazole and 1-imino-2-ethyl-1:2-dihydrobenzthiazole indicate that the error introduced in

this way is of the order of that observed in the analysis of this hydroheptabromide. On reduction with sulphurous acid and sulphur dioxide, the hydroheptabromide yielded 2-*o*-tolylimino-3-*p*(?)-bromo-*o*-tolyl-4-ketotetrahydrothiazole which had m.p. 129° after recrystallisation from alcohol-ethyl acetate. (Found: Br, 27.4. $C_{17}H_{16}ON_2BrS$ requires Br, 27.0 per cent.). This was also obtained (m.p. 126°) by evaporation of the chloroform layers obtained in titration experiments on the hydroheptabromide.

On exposure to air, the hydroheptabromide rapidly lost bromine yielding a bright yellow crystalline *hydrotribromide*, m.p. 132° (decomp.). (Found: Br, 51.6. $C_{17}H_{16}ON_2Br_4S$ requires Br, 52.0 per cent.).

On more than one occasion in our earlier experiments we isolated a red crystalline bromo-addition compound from the bromination of di-*o*-tolyl- ψ -thiohydantoin which had the composition of a hypopentabromide of 2-*o*-tolylimino-3-bromo-*o*-tolyl-4-ketotetrahydrothiazole, m.p. 109-10°. (Found: Br, 61.1. $C_{17}H_{16}ON_2Br_6S$ requires Br, 61.8 per cent.). The low melting point of this substance suggests, however, that it was most probably a eutectic mixture of the hydroheptabromide and hydrotribromide.

s-o-Tolyl-p-bromo-o-tolylthiocarbamide.—A solution of *o*-tolylthiocarbimide (1.2 c.c. in 4 c.c. of alcohol) was added to a solution of *p*-bromo-*o*-toluidine (2.5 g.) in the same solvent (8 c.c.), and the mixture was evaporated on a steam-bath until crystallisation commenced. On recrystallisation from alcohol-ethyl acetate (animal charcoal), the *thiocarbamide* was obtained in soft flaky white crystals, m.p. 152°. (Found: Br, 24.3. $C_{15}H_{15}N_2BrS$ requires Br, 23.9 per cent.). Attempts to synthesise 2-*o*-tolylimino-3-*p*-bromo-*o*-tolyl-4-ketotetrahydrothiazole from this compound by condensation with monochloroacetic acid and pyridine in alcohol led only to gummy resins which could not be investigated.

The authors wish to thank Mr. H. Morland, M.Sc. for carrying out some of the preliminary experiments in connection with this investigation at the Imperial College of Science and Technology, South Kensington in 1926.

The Alkaloids of *Holarrhena Antidysenterica* Part I. Three New Alkaloids from the Bark of Indian *Holarrhena* and New Methods of Isolation and Further Purification of Conessine.

BY SALIMUZZAMAN SIDDIQUI AND P. PARAMESWARAN PILLAY.

A good volume of work has already been done on the different species of *Holarrhena*, resulting invariably in the isolation of conessine ($C_{24}H_{40}N_2$), both from the bark and seeds of the plants. Pyman (*J. Chem. Soc.*, 1919, **115**, 163) isolated from the seeds of *Holarrhena congolensis*, Stapf. another alkaloid, holarrhenine ($C_{24}H_{38}ON_2$, m.p. 197-98°), besides conessine (m.p. 125°, Corr., yield 0.25 p.c.). A little earlier Ulrici (*Arch. Pharm.*, 1918, **256**, 57), working on the bark and seeds of *Holarrhena africana*, had contended to have isolated from conessine melting at 121.5° two different bases, viz., (i) the "true conessine", $C_{23}H_{38}N_2$, cubical crystals, m.p. 125° and (ii) homo-conessine, $C_{25}H_{42}N_2$, (broad needles which begin to soften and effervesce at 50° and have a persistent solid nucleus which does not clear upto 130°), but Giemsa and Halberkann (*Arch. Pharm.*, 1918, **256**, 201), who also worked on the same plant, held them to be identical with conessine as obtained by the previous authors. Ghosh and Ghosh (*J. Indian Chem. Soc.*, 1928, **5**, 477) communicated the isolation of two new alkaloids, kurchicine (m.p. 173°-75°, yield 0.12 p. c.) and kurchine (m.p. 73-75°) besides conessine (m.p. 120°, yield not mentioned).

Owing, on the one hand, to the immense medicinal interest acquired by *Holarrhena antidysenterica* in later years, and on the other, to the amount of controversy that hangs round the problem of its alkaloidal constituents, we found it of interest to undertake a systematic study of the alkaloids of this plant.

As a result of our investigations we have succeeded in obtaining conessine melting at 126° (Corr.) in a yield of 0.4 p.c. on the weight of dry powdered bark and three new alkaloids, viz.,

(i) Conessimine, $C_{23}H_{38}N_2$, m.p. 100°; distils to a crystalline mass at 230°/1.8 mm; $[\alpha]_D^{25} = -22.5^\circ$; $C_{23}H_{38}N_2$, 2 H_2O , m.p. 91°, yield 0.12 p. c.

(ii) Holarrhimine, $C_{21}H_{36}ON_2$, m.p. 183° (Corr.); $[\alpha]_D^{25} = -14.19^\circ$, (yield 0.12 p.c. in fresh and 0.03 p.c. in older bark).

(iii) Holarrhine, $C_{20}H_{38}O_3N_2$, m.p. 240° ; $[\alpha]_D^{25} = -17.01^\circ$. The formula for holarrhine has been assigned only provisionally, as the nitrogen value was too low and the substance did not suffice for a control combustion.

The method which first led to the isolation of conessimine was based on a repeated fractional precipitation of the sulphuric acid soluble portion of the alkaloids with ammonia, whereby the middle fraction gave conessimine in a very low yield as a hydrate fairly insoluble in moist ethyl acetate. A quantitative isolation of it, however, was only possible on exploiting its two very important properties, viz., the formation of its carbonate by passing carbon dioxide into a solution of the different bases in moist petroleum ether, and the insolubility of its hydroiodide in water and alcohol. Conessine, which also forms an insoluble crystalline hydroiodide and belongs to the fraction of weaker bases, does not form a carbonate and can be crystallised out from acetone. The separation of holarrhimine and holarrhine was possible only through a fractional crystallisation of the bases, obtained from the water insoluble crystalline sulphates, out of methyl alcohol-ethyl acetate mixture in which holarrhine is much less soluble than holarrhimine.

Conessimine, is diacidic like conessine, contains one active H and 2 $N-CH_3$ groups and forms a crystalline mononitroso derivative. It thus appears to be a secondary-tertiary base. Holarrhimine, is also diacidic, contains no OCH_3 or $N-CH_3$ group, as against $3N-CH_3$ in holarrhenine, and showed the presence of 3 active H, which could be accounted for by assuming, that it contains 1 OH and 2:NH groups, as this base also gives a non-basic nitroso derivative, which, however, could not be obtained crystalline so far due probably to its being a mixture of mono and dinitroso derivatives.

About the close of our present investigations appeared second part of "The alkaloids of the bark of *Holarrhena antidysenterica*" by Ghosh and Bose (*Arch. Pharm.*, 1932, 270, 100), in which the authors have characterised in detail the two alkaloids, isolated by Ghosh and Ghosh in 1928 (*loc. cit.*). Also, Haworth (*J. Chem. Soc.*, 1932, 631) has communicated the isolation of a new base from the seeds of *Holarrhena antidysenterica* by distilling the mother liquors of conessine, obtained from Simonsen (*J. Chem. Soc.*, 1926, 2123), which he has called norconessine.

In the face of the analytical data and general characteristics of holarrhimine it is quite apparent that it is different from Pyman's holarrhenine, $C_{24}H_{38}ON_2$, m.p. 197° - 98° , $[\alpha]_D = -7.1^{\circ}$.^{*} As to Ghosh's kurehicine, $C_{20}H_{36}ON_2$, m.p. 175° , $[\alpha]_D^{32} = -8.45^{\circ}$, it is either a different base altogether, which we have not yet succeeded in isolating, or a mixture of holarrhimine and holarrhine, as nothing has been done by the authors to separate these two bases, which crystallise together as sulphates.

With regard to conessimine and Ghosh's kurchine, $C_{23}H_{38}N_2$, m. p. 73 - 75° , distilling at $233^{\circ}/1$ mm. to a waxy mass, $[\alpha]_D^{32} = -7.57^{\circ}$, there can be no doubt that the latter, if pure, is quite different from the former. On comparing, however, the methods of isolation of the two bases, it appears more likely that kurchine should prove to be chiefly conessimine in admixture with the non-carbonate forming bases of the conessine group. Also Haworth's norconessine is evidently different from conessimine as the former is a liquid at ordinary temperature, has $[\alpha]_D = +7^{\circ}$ and contains like conessine 3 $N\cdot CH_3$ groups in its molecule as against 2 in conessimine.

As for holarrhine, its melting point and specific rotation are too far apart from those of both kurehicine and holarrhimine to allow of any possibility of its confusion with either.

So far as conessine is concerned we believe to have attained to a higher degree of purity of the base than so far achieved. This was possible through a removal of the last traces of the carbonate-forming, petroleum ether soluble, secondary bases, with nitrous acid, whereby snow-white conessine melting at 126° (Corr.) was obtained. The melting point noted by the different authors for conessine vary from 122° to 125° (Corr.), the latest melting point observed for pure conessine by Späth (*Ber.*, 1930, **63**, 126) being 123° . With regard to the two crystalline forms of conessine, needles and plates, which have formed a source of controversy between Ulrici (*loc. cit.*) and Giemsa and Halberkann (*loc. cit.*), we have incidentally noted, that the plates are the more stable form for conessine.

EXPERIMENTAL.

The material used was obtained from a vaid dealer in drugs in Lahore and identified by the Sibpur Botanical Institute, Howrah.

The dry powdered bark (about a year old) (17 kg.) was percolated eight times with a mixture of 80 parts of ether with 10 parts of alcohol

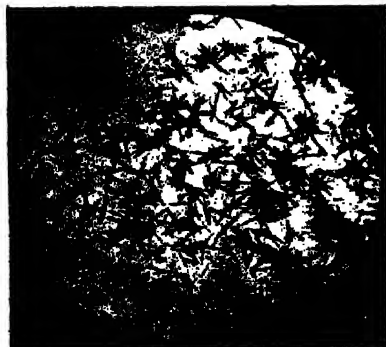
shaken up with 10 parts of liquor ammonia. The percolate was drawn out first after a week and later after every three days, gaseous HCl passed through it till just acid, and the ether decanted off from the precipitated hydrochlorides, made ammoniacal, and used again. After two extractions the ethereal solution decanted from the precipitated hydrochlorides was treated with ammonia and then with acetic acid to faint acidity and the solvent distilled off for further use.

The residue left by the distillation of the extraction medium gave 2 p.c. of neutral matter besides a small quantity of residual alkaloids which was added on to the main alkaloidal hydrochlorides. The total hydrochlorides were dissolved in 2 litres of water and treated with sodium sulphate which gave a cheese-like precipitate of insoluble sulphates, which was filtered and well washed with water. The filtrate from the sulphates was treated with 20 p.c. sodium hydroxide and the alkaloids which were thrown out extracted with ether.

In this way 38 g. of an insoluble sulphate (30 g. free base) and 326 g. of an ether-soluble reddish yellow treacly alkaloids were obtained, giving a yield of 2.1 p.c. of crude alkaloids.

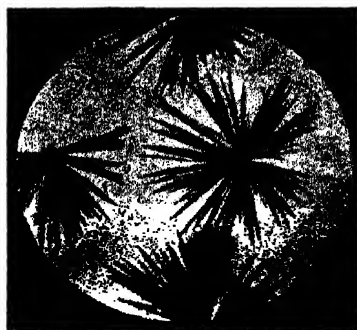
The ether soluble alkaloids were treated with petroleum ether and the soluble portion treated with moist carbon dioxide, which threw down an insoluble carbonate. The petroleum ether insoluble portion was dissolved in ethyl acetate and also separated into carbonate and non-carbonate fractions. After a long process of repeated fractionations, rendered necessary because the separation of the different groups was not very clear cut, the bases were finally separated into three broad fractions: (A) sulphates insoluble in water, (B) carbonates insoluble in petroleum ether, and (C) non-carbonates soluble in petroleum ether.

Fig. 1.



Conessimine.

Fig. 2.



Halarrhimine.

Fig. 8.



Holarrhine.

Isolation of the Bases.

Conessine.—The fraction (C) gave by direct crystallisation from acetone crude conessine (80 g.) which softened at 110° and melted at 110-18°. On recrystallisation out of acetone after removing the last traces of carbonate-forming bases by passing CO₂ into its solution in petroleum ether, suspended over water, conessine which begins to soften at 123° and melts at 124° (yield 68 g.) was obtained. On removing the last traces of secondary bases by treatment with NaNO₂ in acetic acid solution, conessine melting at 126° (Corr.) was obtained, the melting point remaining unaltered on further crystallisation either directly or through its crystalline oxalate.

Conessimine.—The fraction (B) of carbonates was dissolved in hydrochloric acid and fractionally precipitated with ammonia and NaOH. By a repeated fractionation three fractions were finally obtained. The strongest basic fraction gave the residual insoluble sulphates and a fraction of soluble sulphates. The former was added on to the main fraction of sulphates and the base from the latter mixed with the middle fraction. The weakest basic fraction gave some residual conessine and chiefly petroleum ether insoluble carbonates, the base from which was also added on to the middle basic fraction. This was now dissolved in dilute HCl and KI was added to the clear solution in small portions in the cold till the fresh addition of it did not produce any further precipitate. The hydroiodide which came down as a thick oil, soon turned

crystalline (yield 50 g.). After repeated recrystallisations out of a methyl and ethyl alcohol mixture the nearly colourless crystalline hydroiodide, m.p. $308-10^{\circ}$ (decomp.) (pure conessimine hydroiodide melts at $318-19^{\circ}$) was converted into base, which was dissolved in moist petroleum ether and a slow current of CO_2 passed through the solution at ordinary temperature. The base from the precipitated carbonates was dissolved in ethyl acetate, the solution concentrated to a small volume and kept in the cold after adding some water to it, when conessimine hydrate crystallised out in long slender needles. After recrystallisation from the same medium or out of alcohol-water it melted at 91° , turning immediately into a buttery mass, which melts down giving a clear meniscus at 100° , yield 0.12 p.c.

Holarrhine.—The combined insoluble sulphates (38 g.) were treated with 10 p.c. HCl in the cold which dissolved out the major portion, forming a deep red solution. The nearly white, granular residue was then dissolved in hot 10 p.c. methyl alcoholic HCl, the solution neutralised with ammonia and an equal quantity of 1 p.c. H_2SO_4 added to the solution in the hot. On cooling, white silky crystals of the sulphate separated out (yield 10 g.). The base from sulphate, was dissolved in hot methyl alcohol, and ethyl acetate added to the solution till beginning of turbidity. After keeping for a day in the cold a colourless silky crystalline mass separated out, which on recrystallisation out of methyl alcohol and ethyl acetate, yielded holarrhine, m. p. 240° , a subsequent recrystallisation leaving the m.p. unaltered, yield 0.6 g.

Holarrhimine.—On completely removing the solvent from the combined mother liquors of holarrhine, the hot ethyl acetate solution of the residue gave star shaped needles on cooling, m.p. 180° . After repeated recrystallisations from the same solvent holarrhimine was finally obtained, m. p. 183° (Corr.), yield 4 g., 0.03 p.c.

Right in the beginning of the present investigations holarrhimine was isolated with comparatively much greater ease in a yield of 0.12 p. c. out of the fresh bark.

Characterisation of the Alkaloids, their Salts and Derivatives.
Conessimine.

Conessimine crystallised out of its concentrated solutions in dry petroleum ether, ethyl acetate or acetone in microscopic white

needles, m.p. 100°. It is fairly soluble in all the common organic solvents. In 2.606 p.c. solution in chloroform it showed a rotation $[\alpha]_D^{25} = -22.25^\circ$. [Found: C, 80.7, 80.6; H, 11.4, 11.1; N, 8.7; M. W. (cryoscopic in benzene), 358. $C_{23}H_{38}N_2$ requires C, 80.7; H, 11.1; N, 8.2 per cent., M. W., 342]. Out of moist ethyl acetate a sparingly soluble dihydrate of the base crystallises out in long slender needles or oftener in aggregates of short spike formed needles, m.p. 91° (cf. Fig. 1). (Found: C, 72.9; H, 11.0; H_2O , 9.3; $C_{23}H_{38}N_2 \cdot 2H_2O$ requires C, 73.0; H, 11.1; H_2O , 9.5 per cent.).

Conessimine distils at 230°/1.8 mm. to a viscous oil which soon starts crystallising and was found to be the unchanged base, although the rotation was slightly reduced— $[\alpha]_D^{25} = -20.0^\circ$ in chloroform in a concentration of 2.476 p.c.

Dissolved in concentrated H_2SO_4 on a watch glass, conessimine forms a colourless solution, which changes to brilliant yellow after standing for sometime or more quickly on heating for a few minutes on the water-bath. If the watch glass is now exposed to the atmosphere, first a green and then a blue ring begins to develop from the outermost edge of the solution slowly masking its preceding colour towards the centre, giving a rainbow effect to the whole. Finally a pinkish violet ring is noticeable from the outer edge of the blue ring. On gradual addition of drops of water to the original bright yellow solution under stirring, it changes the colours in the same sequence, as observed by Warneke and others in the case of conessine. We found Conessine also to give similar coloured rings as conessimine.

Determination of active H (Zerewitinoff's method) showed the presence of one active H in the molecule. (Found: H, 0.35, $C_{23}H_{38}N_2$ requires H, 0.29 per cent.).

Determination of N-CH₃ (Herzig and Meyer's method) showed the presence of 2 N-CH₃. (Found: CH₃, 8.8. $C_{23}H_{38}N_2$ requires (2N-CH₃) CH₃, 8.8 per cent.).

Conessimine carbonate was obtained on passing CO_2 through a moist petroleum ether solution of the base as a thick voluminous white precipitate, which is soluble in alcohol and insoluble in water and dissolves in dilute acids with effervescence. Dried in the air it begins to soften at 70°, giving off CO_2 , and melts indefinitely upto 105°. It is soluble in cold alcohol and insoluble in petroleum ether saturated with CO_2 , but hot petroleum ether dissolves it owing to decomposition of the unstable salt,

Conessimine hydrochloride, prepared by adding dry ethereal hydrochloric acid to a solution of the base in dry ether, forms a white amorphous powder, is exceedingly soluble in water and alcohol, and showed a rotation in 3.708 p.c. solution in water $[\alpha]_D^{26} = -15.10^\circ$. When dried in *vacuo* at 100° it melts at 342.4° . (Found: Cl, 16.9. $C_{23}H_{38}N_2$, 2 HCl requires Cl, 17.1 per cent.).

Conessimine chloroplatinate, prepared by adding 5 p.c. platinum chloride solution to an aqueous solution of conessimine hydrochloride, formed a cream coloured powder, m.p. 301° (decomp.) and is insoluble in alcohol or water. (Found: Pt, 26.0. $C_{23}H_{38}N_2$, 2 HCl, Pt Cl_4 requires Pt, 25.9 per cent.).

Conessimine aurichloride, obtained as above, forms a yellowish powder, which is insoluble in water and soluble in alcohol. When heated after drying in *vacuo*, it begins to get reddish at 130° , thick red sticky fluid at 140° , and decomposes with evolution of gas at 165° . (Found: Au, 38.3. $C_{23}H_{38}N_2$, 2 HCl, $AuCl_3$ requires Au, 38.6 per cent.).

Conessimine hydroiodide was obtained by adding KI solution to an aqueous solution of the hydrochloride as a thick oil, which quickly turned crystalline. Recrystallised from water it melts at 318.19° (decomp.). (Found: I, 42.9. $C_{23}H_{38}N_2$, 2 HI requires I, 42.6 per cent.).

Conessimine picrate was obtained by adding a concentrated aqueous solution of picric acid to the aqueous solution of the hydrochloride as a brilliant yellow powder, m.p. 172.74° , which is very sparingly soluble in hot water or alcohol, and comes out of the former solvent in stars of long rectangular planks.

Nitrosoconessimine.—To a cooled solution of the base (0.3 g., 1 mol.) in 8 c. c. of 10 p.c. acetic acid was added a concentrated solution of sodium nitrite (0.18 g., 3 mol.) and the reaction mixture was left overnight, when crystalline amber coloured needles (0.24 g.) separated out, which when filtered and washed first with dilute acetic acid and then with water to remove traces of unchanged base, melted at 240.41° (decomp.) after drying in vacuum. (Found: N, 11.9. $C_{23}H_{37}N_2 \cdot NO$ requires N, 11.8 per cent.).

Holarrhimine.

Holarrhimine was precipitated from aqueous solutions of its salts by concentrated ammonia as a gelatinous mass and in a more filterable form by caustic soda solution. It crystallised out of ethyl

acetate in colourless star-shaped radiating needles (cf. Fig. 2), m.p. 183° (Corr.). It is very soluble in alcohol and chloroform and almost insoluble in ether and petroleum ether. In 4.793 p. c. chloroform solution it shows a rotation of $[\alpha]_D^{25} = -14.19^\circ$. The rotation was found to diminish on long treatment of the base with hydrochloric acid. After drying in *vacuo* at 100° the base gave the following analysis. (Found: C, 75.6, 75.8; H 11.1, 11.0; N, 8.3. $C_{21}H_{36}ON_2$ requires C, 75.9; H, 10.8; N, 8.4 per cent.).

Holarrhimine is a diacid base, has no OCH_3 or $N-CH_3$ group, but shows the presence of three active H. (Found: H, 0.88. $C_{21}H_{36}ON_2$ requires H, 0.90 per cent.).

Holarrhimine carbonate separated out as a bulky amorphous powder on dissolving the base in moist ethyl acetate and passing CO_2 through the solution. When washed with ethyl acetate saturated with CO_2 and dried in the air it begins to give off CO_2 from 80° upwards without showing any definite sign of melting. It dissolves in acids with effervescence, is fairly soluble in alcohol and insoluble in other organic solvents in the cold.

Holarrhimine hydrochloride was prepared by adding ethereal hydrochloric acid to a chloroformic solution of the base, m. p. 345° (decomp.). It is very soluble in alcohol, less so in water, and sparingly soluble in 10 p. c. aqueous or alcoholic HCl. It crystallises from water in star-like aggregates of broad plates. In 2.193 p. c. methyl alcoholic solution it shows a rotation of $[\alpha]_D^{25} = -22.80^\circ$. (Found: Cl, 17.2. $C_{21}H_{36}ON_2 \cdot 2HCl$ requires Cl, 17.5 per cent.).

Holarrhimine chloroplatinate, prepared as in case of conessimine, forms a cream coloured powder, insoluble in alcohol or water, darkens at 270° and chars above 300° without melting. (Found: Pt, 26.2. $C_{21}H_{36}ON_2 \cdot 2HCl \cdot PtCl_4$ requires Pt, 26.3 per cent.).

Holarrhimine hydrobromide was prepared by dissolving the base in dilute HBr and allowing it to cool, when it came out as a crystalline mass. On recrystallisation out of water in which it is sparingly soluble it formed star-shaped aggregates of thin plates and broad needles, m. p. 358-60° (decomp.).

Holarrhimine picrate, prepared by adding dry ethereal picric acid to an alcoholic solution of the base, formed a heavy crystalline powder, m. p. 198-200° (decomp.). It crystallises from hot water, in which it is fairly soluble, in brilliant yellow plates with a silky lustre, apparently in hydrated form (m. p. 108-10°).

Holarrhimine sulphate was prepared by dissolving the hydrochloride in methyl alcohol and adding dilute sulphuric acid to the solution till beginning of turbidity at water-bath heat, when it soon crystallised out in snow-white silky needles and spangles, m. p. 337°. It is almost insoluble in water and all the organic solvents.

Holarrhine.

Holarrhine crystallised from a mixture of methyl alcohol and ethyl acetate in white needles, m. p. 240°. It is very soluble in methyl and ethyl alcohols, sparingly so in chloroform, and almost insoluble in ethyl acetate, ether and petroleum ether. (Found: C, 67·4; H, 10·3; N, 6·5. $C_{20}H_{18}O_3N_2$ requires C, 67·8; H, 10·7; N, 7·9 per cent.). In 4·992 p. c. methyl alcoholic solution, it shows a rotation of $[\alpha]_D^{25} = -17·01^\circ$. It gives a distinct precipitate on addition of sodium nitrite solution into its acetic acid solution and so appears to be a secondary base.

Holarrhine chloroplatinate was obtained on addition of a cooled 3 p. c. platinic chloride solution to a cooled aqueous solution of the hydrochloride as a yellowish amorphous powder darkening from 270° onwards, and charring above 300°. (Found: Pt, 25·4. $C_{20}H_{18}O_3N_2 \cdot 2HCl \cdot PtCl_4$ requires Pt, 25·5 per cent.).

Holarrhine picrate, prepared as in case of holarrhimine, formed a pale yellow semi-crystalline powder which begins to darken at 275°, but does not melt upto 320°.

Conessine.

Conessine crystallises out of acetone in large prismatic plates, but from more dilute solutions as long flat needles or aggregates of shorter needles, if allowed to crystallise slowly and completely undisturbed. On stirring, however, the needles abruptly changes into plates. If carefully dried, the needles can be collected as such and show the same m. p. as the plates. (Found: C, 80·9; H, 11·3. $C_{24}H_{40}N_2$ requires C, 80·8; H, 11·3 per cent.).

Conessine hydrochloride, prepared by adding ethereal HCl to a solution of the base in dry ether, formed a white powder, which browned up at 335° and melted at 338-40° (decomp.).

Conessine hydroiodide, prepared like conessimine hydroiodide, formed long colourless bars, m. p. 308° (decomp.). (Found: I, 41·2. $C_{24}H_{40}N_2 \cdot 2HI$ requires I, 41·6 per cent.). It is difficultly soluble in

water, fairly soluble in methyl alcohol, less so in ethyl alcohol and in other organic solvents.

Conessine picrate was obtained by adding ethereal picric acid to a dry ethereal solution of the base as a brilliant yellow semi-crystalline powder m. p. 222-24° (decomp.). It crystallises out of hot water in stars of crowded needles.

Conessine oxalate, prepared by dissolving the base in 10 p. c. aqueous oxalic acid, formed a white crystalline powder which on recrystallisation out of water melted at 372° (decomp.).

• *Colour reactions of the alkaloids of Holarrhena antidysenterica.*

Reagent.	Conessimine.	Conessine.	Holarrhimine.	Holarrhine.
Conc. H_2SO_4	Colourless; after standing for $\frac{1}{2}$ hr. or on warming for about 5 min. bright golden yellow to orange; on addition of water, violet.	Same as conessimine.	Yellowish red; then bright red; water lightens colour.	• Same as holarrhimine.
HNO_3	Colourless	Do	Colourless	Do
Conc. H_2SO_4 and $K_2Cr_2O_7$	Yellowish green to deep green according to concentration; on adding water colour lightens.	Same as conessimine.	Deep green, water lightens colour.	Same as holarrhimine.
Erdmans reagent	Golden yellow; on adding drops of water turns successively green, blue and then violet.	Do	Deep red	Do
Froehde reagent	Grass green, then deep green; colour lightens on addition of water.	Do	Yellowish green; on warming brown with a greenish yellow tinge; on adding a little water deep reddish brown, on further dilution deep red.	

Metallic Cerium in Organic Synthesis.

BY JAGARAJ BEHARI LAL AND SIKHIBHUSHAN DUTT.

Since the middle of the nineteenth century various metals, *e.g.*, sodium, potassium, silver, zinc, copper, mercury, magnesium, aluminium, etc., have been used more or less successfully in organic synthesis, but the metal cerium which has been a chemical curiosity for quite a long time and whose commercial manufacture has been of comparatively very recent origin, has not received any application in organic synthesis upto this time. Consequently the present investigation was undertaken. Details of the successful experiments are given in the experimental part, while those of the unsuccessful attempts are omitted.

EXPERIMENTAL.

Dry distillation with cerium powder.—In these experiments various organic compounds were submitted to dry distillation with cerium powder in a current of pure hydrogen in accordance with the method already described by Ray and Dutt (*J. Indian Chem. Soc.*, 1928, 5, 103 ; *cf.* also Chakrabarty and Dutt, *ibid.*, p. 513). The results are summarised in the table below.

Substance.	Temperature of distillation.	Main product.	Yield.	By-products.
Phenol	470°	benzene	39%	diphenyl
Resorcinol	500°-540°	„	42	phenol
Hydroquinone	„	„	40	„
Pyrogallol	„	„	27	phenol, catechol
α -Naphthol	„	naphthalene	60	nil
β -Naphthol	„	„	66	nil
α -Nitronaphthalene	„	α -naphthylamine	49	naphthalene
<i>p</i> -Nitrotoluene	„	<i>p</i> -toluidine	33	toluene
Salicylic acid	„	benzene	51	phenol
Phthalic anhydride	dull red heat	phthalide	12	benzaldehyde
Benzoic acid	„	benzene	30	diphenyl

Substance.	Temperature of distillation.	Main product.	Yield.	By-products.
<i>p</i> -Nitrophenol	dull red heat	aniline	32%	<i>p</i> -aminophenol
<i>o</i> -Nitrophenol	"	"	37	<i>o</i> -aminophenol
Azobenzene	"	"	32	nil
Anthraquinone	"	anthracene	61	nil
Phenanthraquinone	"	phenanthrene	54	nil
<i>p</i> -Nitroaniline	400°	<i>p</i> -phenylenediamine	32	aniline
Benzophenone	"	diphenylmethane	59	nil
Thiodiphenylamine	dull red heat	carbazole	56	hydrogen sulphide

Friedel and Craft's Reaction with Cerium Powder.

Triphenylmethane from benzal chloride and benzene.—Benzene (18.7 g.), benzal chloride (8.6 g.) and cerium powder (5 g.) were refluxed together on a water-bath for 10 hours. The dark violet product was filtered from the excess of cerium and fractionated to remove benzene and benzal chloride. The solid residue crystallised from alcohol in needles, m. p. 92° and was identified to be triphenylmethane, yield 1.2 g.

Triphenyl carbinol from benzoyl chloride and benzene.—A mixture of benzene (50 g.), benzoyl chloride (15 g.) and cerium powder (4 g.) was heated under reflux for 15 hours. Dark red product was fractionated as above and the fraction above 250° crystallised in yellow needles from alcohol, m. p. 160° and identified as triphenyl carbinol, yield 7.2 g.

Benzoylbenzoic acid from benzoyl chloride and benzoic acid.—Benzoyl chloride (7.5 g.), benzoic acid (6 g.) and cerium powder (4 g.) were refluxed at 160° for 12 hours. The dark violet product was treated with dilute hydrochloric acid and steam distilled until benzoic acid ceased to come over. The hot filtrate deposited needles of *o*-benzoylbenzoic acid on cooling, m. p. 128°, yield 5.1 g.

Triphenylchloromethane from benzotrichloride and benzene.—Benzotrichloride (6.8 g.), benzene (20 g.) and cerium powder (8 g.) were heated under reflux for 14 hours. The dark red product was fractionated at 15 mm. from an oil-bath at 150° until nothing further distilled over. The solid residue crystallised from carbon disulphide in pale yellow prisms, m. p. 106° and was identified to be triphenylchloromethane, yield 1.5 g.

Diphenyl from benzene and bromobenzene.—Benzene (12 g.), bromobenzene (8.5 g.) and cerium powder (4 g.) on refluxing for 20 hours gave very feeble reaction. The yield of diphenyl isolated on fractionation was only 0.25 g., m. p. 68°.

Diphenyl from chlorobenzene and benzene.—Reaction was carried on as above. Yield of diphenyl from 11 g. of chlorobenzene was only 0.8 g.

Diphenyl from iodobenzene and benzene.—Reaction was carried on as above. Yield of diphenyl from 8.1 g. of iodobenzene was only 0.22 g.

Triphenylmethane from benzene and chloroform.—Benzene* (18 g.), chloroform (18 g.) and cerium powder (4 g.) were refluxed for 12 hours. The dark violet product was fractionated first at ordinary pressure and then at 8 mm. over naked flame. The last product solidified on cooling and crystallised from alcohol, m. p. 92° and identified to be triphenylmethane, yield 2.6 g.

Anthraquinone from benzene and phthalyl chloride.—Phthalyl chloride (10 g.), benzene (12 g.) and cerium powder (4 g.) were refluxed at 170-80° for 6 hours. The reaction mixture was treated with dilute hydrochloric acid to remove cerium and with dilute caustic soda to remove phthalic acid. The benzene was distilled off and residual anthraquinone crystallised from acetic acid, m. p. 276°, yield 3.5 g.

Benzylidene acetophenone from benzal chloride and acetophenone.—A mixture of acetophenone (3 g.), benzal chloride (4 g.) and cerium (1.2 g.) when refluxed at 180-200° for 4 hours gave a very vigorous reaction and the product on alcohol extraction yielded a crystalline solid. It was recrystallised from ligroin and identified as benzylidene acetophenone, m. p. 57°, yield 3 g.

Zincke's Reaction with Cerium Powder.

Diphenylmethane from benzyl chloride and benzene.—Benzene (88.5 g.), benzyl chloride (20 g.) and cerium (5.2 g.) were refluxed for 10 hours. The dark red product was filtered, washed with water, dried and fractionated. The fraction between 250-80° (11.2 g. redistilled at 260-62°) was collected and identified to be diphenylmethane. Lower fractions contained benzene and benzyl chloride and the higher fractions triphenylmethane and sym-tetraphenylethane, (4.2 g. and 1.5 g. respectively).

Phenyltolylmethane and dibenzyltoluene from benzyl chloride and toluene.—A mixture of benzyl chloride (25.8 g.), toluene (34 g.) and cerium (6 g.) was refluxed at 110-20° for 10 hours. The product was purified and fractionated as above. The fraction at 260-85° (redistilled at 275-82° and then again at 279-80°) was identified to be phenyltolylmethane (yield 23.1 g.) and that above 310° (subsequently redistilled at 390-98°) as dibenzyltoluene (12.4 g.).

Anisoylphenylmethane from anisol and benzyl chloride.—Anisol (22 g.), benzyl chloride (21 g.) and cerium powder (5 g.) were refluxed at 110-20° for 8 hours. The mixture was purified and fractionated as above. The fraction at 300-15° (redistilled at 305-10°) was identified to be anisoylphenylmethane *i.e.* *p*-methoxydiphenylmethane (yield 18.8 g.) and the fraction at 378-80° (9.2 g.) was most probably dibenzylanisol but could not be identified for want of accurate information.

Phenetoylphenylmethane from phenetol and benzyl chloride.—A mixture of phenetol (20.4 g.), benzyl chloride (18.2 g.) and cerium (5 g.) were treated as above, and the reaction product similarly fractionated. The fraction at 312-45° (redistilled at 338-41°) was identified to be *p*-ethoxydiphenylmethane (yield 26.8 g.). The dark red residue in the distilling flask crystallised from alcohol in bright yellow plates, m.p. 57° and was probably dibenzylphenetol, but could not be identified for want of data (yield 2.1 g.).

Benzylquinol dimethyl ether from benzyl chloride and quinol dimethyl ether.—Quinol dimethyl ether (14 g.), benzyl chloride (10 g.) and cerium (5 g.) were refluxed at 120-30° for 10 hours. The product was purified and fractionated as above and the fraction at 345-60° (redistilled at 354-56°) identified as benzylquinol dimethyl ether, yield 14.2 g.

p-Benzylphenol from benzyl chloride and phenol.—Benzyl chloride (16 g.), phenol (21 g.) and cerium (6.2 g.) were heated at 70° for $\frac{1}{2}$ hour and then at 120-30° for 6 hours. Reaction was very vigorous. The product was purified and fractionated as above. The fraction at 310-30° (redistilled at 320-22°) was identified as *p*-benzylphenol (yield 27.6 g.) and the fraction at 360-70° (redistilled at 365-67°) which was free from phenolic group was identified as *p*-benzylphenol benzyl ether, $C_6H_5CH_2 \cdot C_6H_4 \cdot O \cdot CH_2C_6H_5$, yield 3.2 g.

Acetophenone from acetyl chloride and benzene.—Benzene (16 g.), acetyl chloride (12 g.) and cerium (4 g.) when refluxed for 6 hours gave a very vigorous reaction. The product was treated with ice-cold

hydrochloric acid and the resulting yellow oil washed, dried and fractionated. The fraction at 185°-210° (redistilled at 198-200°) was identified as acetophenone, yield 12.2 g.

Benzophenone from benzoyl chloride and benzene.—On refluxing a mixture of benzoyl chloride (10.2 g.), benzene (15 g.) and cerium (8.5 g.) for 12 hours, the product was filtered, washed with strong caustic soda and water, dried and fractionated. The fraction at 300-15° solidified in the receiver and after recrystallisation from alcohol (m. p. 47°) it was identified as benzophenone, yield 2.9 g.

Reformatski's Reaction with Cerium Powder.

A mixture of acetophenone (12 g.), ethyl chloroacetate (12 g.), cerium (10 g.) and dry benzene (70 g.) was refluxed with the addition of a minute crystal of iodine for 2 hours. Reaction was very vigorous. The product was treated with ice-cold dilute hydrochloric acid, washed with sodium hydroxide and water, dried and fractionated at 5 mm. The fraction at 112-30° (redistilled at 118-20°) was identified as β -phenylmethylhydroxypropionic ester, yield 6.1 g.

The above reaction was tried with ethyl bromoacetate instead of ethyl chloroacetate, yield 9.3 g.

Ullmann's Reaction with Cerium Powder.

Diethyl succinate from ethyl chloroacetate and ethyl acetate.—A mixture of ethyl chloroacetate (12 g.), ethyl acetate (10 g.) and cerium (3 g.) was refluxed at 110-20° for 12 hours and the product filtered, washed, dried and fractionated. The fraction at 200-20° (redistilled at 216-18°) was identified as diethyl succinate, yield 3.8 g.

Adipic acid from β -iodopropionic acid.—When β -iodopropionic acid (5 g.) was heated with cerium (8 g.) at 160-70° for 3 hours much iodine liberated. The product was extracted with hot water and the aqueous solution on concentration gave adipic acid crystal, m.p. 148°, yield 0.7 g.

Diphenyl from bromobenzene.—Bromobenzene (8 g.) and cerium (12 g.) were refluxed at 170-80° for 20 hours. The product was filtered and fractionated. The fraction at 240-60° (redistilled at 252-54°) solidified on cooling and recrystallised from ether, m.p. 70°, and was identified as diphenyl, yield 0.75 g.

Diphenyl from (i) iodobenzene and (ii) chlorobenzene.—Procedure was same as above, yields of diphenyl isolated, 0.5 g. from (i) and 0.28 g. from (ii).

Diphenyl ether from phenol and bromobenzene.—A mixture of phenol (9.5 g.), bromobenzene (17 g.), cerium (5 g.) and anhydrous potassium carbonate (0.5 g.) was refluxed at 180-200° for 10 hours. The filtered product was steam distilled and the distillate was extracted with ether. The extract was washed with dilute caustic soda and water, dried and fractionated. The fraction at 240-60° (redistilled at 253-54°) was identified as diphenyl ether, yield 3.5 g.

Diphenylamine from aniline and bromobenzene.—Aniline (12 g.), bromobenzene (16 g.) and cerium (3 g.) were refluxed at 180-200° for 10 hours. The filtered product was fractionated and the fraction at 300-20° solidified, and recrystallised from alcohol, m. p. 52°, and identified as diphenylamine, yield 2.8 g.

Succinic acid from chloroacetic and acetic acids.—A mixture of sodium chloroacetate (11.5 g.), anhydrous sodium acetate (8 g.) and cerium (4 g.) when heated at 110-20° for 1 hour gave a very vigorous reaction. The product was extracted with water and ammonia added in slight excess to precipitate ceric hydroxide. The boiled and neutral filtrate was treated with ferric chloride when ferric succinate was precipitated. This was decomposed in aqueous suspension by hydrogen sulphide and from the filtrate succinic acid was extracted with ether, m.p. 185°, yield 2.9 g.

Neutral Reduction with Cerium Powder.

Picramic acid and triaminophenol from picric acid.—Picric acid (10 g.) in alcohol (70 p.c.) containing ammonium chloride (4.5 g.) was vigorously shaken with cerium powder (25 g.) in a shaking machine. After 10 hours the product was completely reduced and yielded 63 p.c. of triaminophenol. After 5 hours the product consisted of a mixture of picramic acid (85 p.c.) and triaminophenol (5 p.c.).

Sulphanilic acid and dimethylaniline from methyl orange.—Methyl orange (6.5 g.), water (1500 c.c.), cerium (15 g.) and ammonium chloride (3.5 g.) were shaken together for 3 hours. The product resolved into sulphanilic acid (2.1 g.) and dimethylaniline (1.9 g.) with complete reduction.

o-Aminophenol from o-nitrophenol.—o-Nitrophenol on similar treatment as above yielded o-aminophenol (79 p.c.).

Benzhydrol from benzophenone.—Benzophenone (6 g.), alcohol (150 c.c., 70 p.c.), ammonium chloride (3 g.) and cerium (6 g.)

were shaken for 20 hours. 5.4 G. of benzhydrol (m.p. 66°) were obtained.

Aniline from nitrobenzene.—Nitrobenzene (6 g.), ammonium chloride (0.5 g.), water (100 c.c.) and cerium (16 g.) were shaken for 4 hours, then warmed on the water-bath for 1 hour with addition of more cerium (12 g.). Yield of aniline 3.5 g.

p-Toluidine from nitrotoluene.—*p*-Nitrotoluene on similar treatment as above yielded *p*-toluidine (66 p.c.).

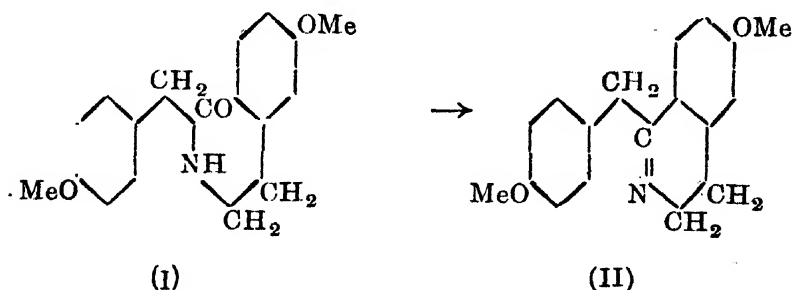
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A New Synthesis of 3:10-Dimethoxytetrahydroprotoberberine.

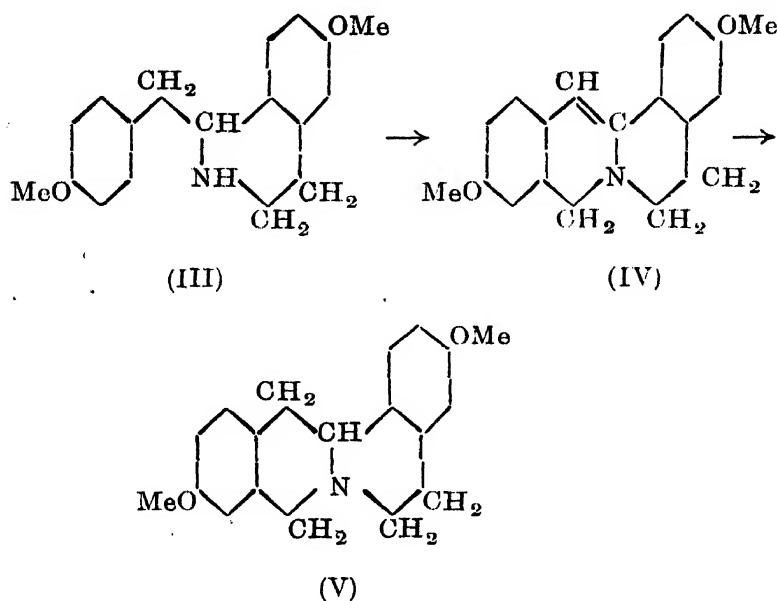
BY SATYENDRA NATH CHAKRAVARTI, N. ANANTHA VAIDYANATHAN
AND A. VENKATASUBBAN.

3:10-Dimethoxytetrahydroprotoberberine (V), which had previously been prepared by one of us (Chakravarti and Perkin, *J. Chem. Soc.*, 1929, 196) has now been synthesised by a method similar to that used for the synthesis of 3:11-dimethoxytetrahydroprotoberberine (Chakravarti, Haworth and Perkin, *ibid.*, 1927, 2265). β -m-Methoxyphenylethylamine, prepared by a slight modification of the method previously described (*J. Chem. Soc.*, 1927, 2269) was condensed with *p*-methoxyphenylacetic acid (prepared by a modification of the method of Mauthner, *Annalen*, 1909, 370, 374 ; Wakeman and Dakin, *J. Biol. Chem.*, 1911, 9, 150; Cain, Simonsen and Smith, *J. Chem. Soc.*, 1913, 103, 1036) and *p*-methoxyphenylaceto- β -m-methoxyphenylethylamide (I) (m.p. 81°) was converted in a yield of more than 80% into 6-methoxy-1(4'-methoxybenzyl)-3:4-dihydroisoquinoline (II). The base readily forms a hydrochloride and a picrate and oxidises rapidly on exposure to air and is readily



reduced by zinc and sulphuric acid to 6-methoxy-1(4'-methoxybenzyl)-1:2:3:4-tetrahydroisoquinoline (III), a base yielding a crystalline sulphate and picrate. Attempts to convert (III) into 3:10-dimethoxytetrahydroprotoberberine by means of formaldehyde were unsuccessful, invariably gummy products being obtained. It was ultimately found that treatment of the *N*-formyl derivative of (III) with phosphorus oxychloride gave 3:10-dimethoxydihydroprotoberberine (IV)

in 20% yield. The substitution of phosphorus pentoxide for the oxychloride did not effect any improvement in the yield. The base (IV) was not isolated as such, except in a preliminary experiment, but directly reduced by zinc dust and hydrochloric acid to 3:10 dimethoxytetrahydroprotoberberine (V), m.p. 139°. A mixed melting point with a specimen synthesised by the



previous method (*J. Chem. Soc.*, 1929, 201) caused no depression.

The interesting point which arises from this investigation is that whilst the first cyclisation, that is to say, the conversion of (I) into (II) takes place readily, the second cyclisation, *i.e.*, the conversion of (III) into (IV) takes place with much less readiness. This is undoubtedly due to the presence of a *para* activating methoxy group in (I), and the absence of such a group in (III).

EXPERIMENTAL.

p-Methoxyphenylaceto-*m*-methoxyphenylethylamide, (I).—*β*-*m*-Methoxyphenylethylamine was prepared by a slight modification of our previous method (*loc. cit.*), the modification consisting in methylating *m*-hydroxybenzaldehyde by shaking it with slight excess of dimethyl sulphate in alkaline solution and then heating the product for 1 hour on the water-bath. Thus the use of methyl alcohol was

obtained and a 90 per cent. yield of *m*-methoxybenzaldehyde was obtained.

In preparing *p*-methoxyphenylacetic acid the following modification was used:

The azlactone obtained by the condensation of anisaldehyde and hippuric acid was hydrolysed by means of 10 p. c. sodium hydroxide solution, and the alkaline solution was then saturated with sulphur dioxide, the benzoic acid collected, and the filtrate acidified and boiled. *p*-Methoxyphenylpyruvic acid which gradually separated was collected and crystallised from glacial acetic acid. This acid (m.p. 192°) was oxidised in cold alkaline solution with hydrogen peroxide. On acidifying the solution, *p*-methoxyphenylacetic acid, m.p. 86°, separated in beautiful plates and in an excellent yield.

Equivalent quantities of β -*m*-methoxyphenylethylamine and *p*-methoxyphenylacetic acid were heated at 180° for 2 hours. On crystallising the product from benzene through the aid of animal charcoal, *p*-methoxyphenylaceto- β -*m*-methoxyphenylethylamide (I) was obtained as colourless plates, m.p. 81°, in a good yield. (Found: C, 72.0; H, 7.2. $C_{18}H_{21}O_3N$ requires C, 72.2; H, 7.0 per cent.).

6-Methoxy-1(4'-methoxybenzyl)-3,4-dihydroisoquinoline, (II).—The amide (I) (10 g.) was heated with phosphorus oxychloride (25 c.c.) for 2 hours on the steam-bath and then kept overnight. The mixture was decomposed with cold water and the clear solution thus obtained was basified with sodium hydroxide in presence of benzene in a separating funnel, the precipitate formed being immediately shaken up with benzene. The alkaline solution was once more extracted with benzene and part of the combined benzene extract (A) was dried over potassium carbonate, and concentrated to a small bulk when a colourless oil was obtained.

A crystalline hydrochloride and a crystalline picrate, m.p. 146° (Found: C, 56.3; H, 4.6. $C_{24}H_{22}O_9N_4$ requires C, 56.5; H, 4.3 per cent) was prepared from the above base by usual methods.

6-Methoxy-1(4'-methoxybenzyl)-1:2:3:4-tetrahydroxyisoquinoline, (III) was obtained by extracting the benzene extract (A) with dilute sulphuric acid, and reducing the acid solution with zinc dust. On cooling, the crystalline sulphate was deposited in the form of plates. The sulphate was dissolved in water and decomposed with ammonia, and the tetrahydro base extracted with chloroform, dried over potassium carbonate and the solvent removed, leaving the base as an oil. The hydrochloride, obtained by dissolving the oil in hot

dilute hydrochloric acid, and cooling, separated as a crystalline powder, m.p. 196° . (Found: C, 67.4; H, 7.1. $C_{18}H_{22}O_2NCl$ requires C, 67.6; H, 6.9 per cent.). The picrate prepared in alcoholic solution is sparingly soluble in cold alcohol and separated from this solvent as a crystalline powder, m.p. 192° (decomp.).

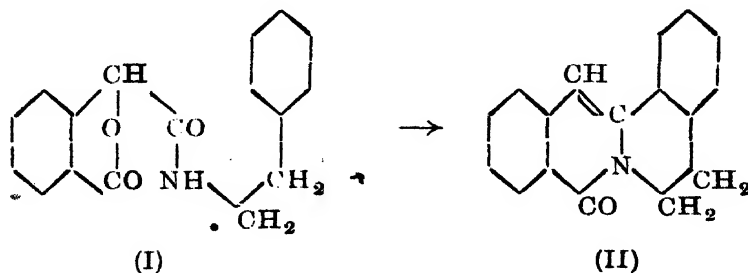
3:10-Dimethoxytetrahydroprotoberberine, (V).—This base could not be obtained by treating the foregoing base with formaldehyde in the usual manner. This base was obtained in a 20 per cent. yield by the following method. The base (III) was heated with equivalent amount of anhydrous formic acid in an oil-bath at $200-10^{\circ}$ until effervescence had ceased (3 hours). The product was dissolved in toluene and boiled with phosphorus oxychloride for $1\frac{1}{2}$ hours. After remaining overnight light petroleum was added and the clear liquid decanted from the dark coloured gum, the latter extracted with dilute hydrochloric acid (charcoal), and the solution of dihydroprotoberberine reduced by heating with excess of zinc dust for 2 hours, during which the yellow solution became colourless. The hot liquid was filtered, the filtrate decomposed with ammonia, the base extracted with chloroform, dried over potassium carbonate, the chloroform removed, and the residue crystallised from methyl alcohol. On recrystallisation from methyl alcohol with the aid of animal charcoal, the substance was obtained in beautiful prisms, m.p. 139° . (Found: C, 77.1; H, 7.3. $C_{19}H_{21}O_2N$ requires C, 77.3; H, 7.1 per cent.).

In a preliminary experiment, an attempt was made first to get 3:10-dimethoxydihydroprotoberberine (IV) in a crystalline state and then to reduce it to (V). It was found, however, that 3:10-dimethoxydihydroprotoberberine (IV), crystallised much less readily than 3:10-dimethoxytetrahydroprotoberberine (V).

An Attempted Synthesis of Oxyptoberberine and a Synthesis of 3-Methoxyoxyptoberberine.

By SATYENDRA NATH CHAKRAVARTI AND A. P. MADHAVAN NAIR.

An unsuccessful attempt to synthesise oxyptoberberine and tetrahydroprottoberberine, the parent substance of the berberine and palmatine group of alkaloids, for which the name "Berbin" has recently been suggested by Walter Awe (*Arch. Pharm.*, 1932, 270, 161), was first made by Haworth, Perkin and Pink (*J. Chem. Soc.*, 1925, 127, 1711). These compounds were first synthesised by one of us (S.N.C.) in 1927 (*J. Chem. Soc.*, 1927, 2275). The melting point of tetrahydroprottoberberine was found to be 85°, and numerous derivatives of this compound were prepared. In the same year Kitasato prepared a compound having the melting point 254-60°, which he called tetrahydroprottoberberine (*Acta Phytochim.*, 1927, 3, 175). In view of this discrepancy, we sought to verify our results by synthesising tetrahydroprottoberberine by another method analogous to that employed by Perkin, Ray and Robinson for synthesising oxyberberine (*J. Chem. Soc.*, 1925, 127, 740). For this purpose the acid chloride of phthalide-carboxylic acid was condensed with β -phenylethylamine when the amide (I) (m.p. 155°) was formed. Unfortunately all attempts to convert the amide (I) into oxyptoberberine (II) were unsuccessful, undoubtedly due to the absence of



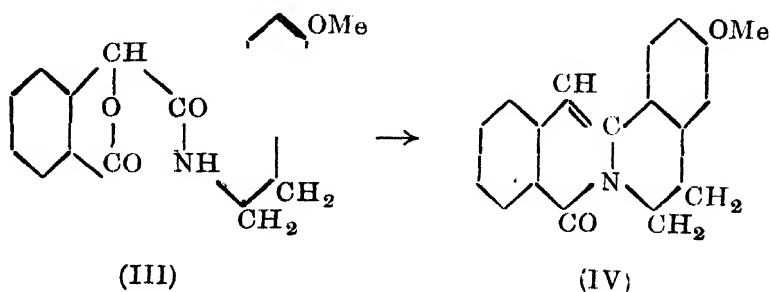
activating methoxy groups. When phosphorus pentachloride was used to effect cyclisation in place of phosphorus oxychloride,

crystalline substance (m.p. 153°) was obtained in a poor yield. This substance was found to be quite different from oxyprotoberberine synthesised previously and its analysis did not agree with the values calculated for oxyprotoberberine.

While these experiments were in progress, Wolfgang Leithe published a paper which fully confirmed the results obtained previously by one of us (S.N.C.). He synthesised tetrahydroprotoberberine anew by a slight modification of our previous method and found its melting point to be 85° (*Ber.*, 1930, **63**, 2343). In view of this work, and the fact that Kitasato withdrew his statement in a private communication to one of us, further work on this subject was discontinued.

Incidentally, 3-methoxyoxyprotoberberine (IV) was synthesised, a synthesis which is of interest from the point of view of the determination of ease of formation of alkaloids of berberine-palmatine type containing no pyrocatechol nuclei (*cf.* Chakravarti, Haworth and Perkin, *J. Chem. Soc.*, 1927, 2267, 2275; Chakravarti and Perkin, *ibid.*, 1929, 196).

The acid chloride of phthalide-carboxylic acid condensed readily in benzene solution with β -*m*-methoxyphenylethylamine yielding phthalide-carboxy- β -*m*-methoxyphenylethylamide (III), m.p. 105° . When this was heated with phosphorus oxychloride and the product decomposed with ice, a basic substance separated (on basification of the aqueous solution), which, on reduction with zinc dust and acetic acid, was converted into a pale yellow substance, m.p. 143° , having all the properties of a compound of the oxyberberine type, and this is doubtless the 3-methoxyoxyprotoberberine (IV).



The point of general interest which emerges from this synthesis is that the synthetical experiments described proceed as readily when

only one methoxy group is present in the *meta* position to ethylamine group, as they do in the case of the corresponding syntheses in the berberine group. The ease of formation in this case is doubtless due to the presence of an activating *para*-methoxy group.

EXPERIMENTAL.

Phthalide-carboxy-β-phenylamide, (I).—Phthalide carboxylic acid (10 g.) prepared by the reduction of phthalonic acid which in its turn was prepared by the oxidation of naphthalene (Compare Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1805; Graebe and Trumpy, *Ber.*, 1898, **31**, 373), was thoroughly mixed with the equivalent amount of phosphorus pentachloride and heated on the steam-bath for 3 hours. Phosphorus oxychloride formed was then completely removed by distillation in *vacuo*, and the residue dissolved in dry benzene and added gradually to a dry benzene solution of β-phenylethylamine (prepared from 9 g. of the hydrochloride). After remaining overnight, the mixture was heated on the steam-bath for $\frac{1}{2}$ hour, cooled, and washed successively with sodium carbonate solution and dilute hydrochloric acid, and dried over sodium sulphate. On distilling off most of the benzene, the amide separated as a white powder (yield almost quantitative). On repeated recrystallisations from ethyl alcohol it melts at 155°. (Found: C, 72·8; H, 5·3. $C_{17}H_{15}O_3N$ requires C, 72·6; H, 5·3 per cent.).

An attempted synthesis of oxyprotoberberine, (II).—An attempt was made to convert phthalide-carboxy-β-phenylethylamide (I) into oxyprotoberberine, by treating the amide with phosphorus oxychloride and then treating the basic substance thus formed with zinc dust and glacial acetic acid exactly under conditions described by Perkin, Ray and Robinson (*loc. cit.*) for converting the piperonylethylamide of meconine carboxylic acid into oxyberberine (*cf.* Chakravarti and Perkin, *loc. cit.*). The final product obtained was a brown resinous substance which could not be obtained in a crystalline form, and which could not be further examined owing to the very poor yield. Phosphorus pentoxide in boiling xylene solution was then tried as the cyclising agent. Again a very poor yield of the same resinous substance was obtained. When, however, phosphorus pentachloride was used as the cyclising agent, a distinctly crystalline pale yellow substance was obtained, which was repeatedly crystallised from methyl

alcohol in beautiful needles, m. p. 153° , and is very readily soluble in the usual organic solvents. (Found: C, 72.2; H, 4.45; N, 4.8. $C_{17}H_{13}ON$ requires C, 82.6; H, 5.3; N, 5.7 per cent.). We are indebted for this microanalysis to Dr. Ing. A. Schoeller of Berlin.

The substance thus formed differs markedly in its properties from oxyprotoberberine synthesised by one of us (*J. Chem. Soc.*, 1927, 2280), and it could not be further investigated owing to the small amount of the substance at our disposal.

Phthalide-carboxy- β -m-methoxyphenylethylamide, (III).— β -m-Methoxyphenylethylamide was prepared by a slight modification of the method previously described by one of us (Chakravarti, Haworth and Perkin, *loc. cit.*), *m*-hydroxybenzaldehyde being methylated in the following manner in more than 90 per cent. yield. 50 G. of *m*-hydroxybenzaldehyde dissolved in 200 c. c. of 10 p.c. sodium hydroxide solution, was treated gradually with constant shaking with 55 c.c. of dimethyl sulphate. When all the dimethyl sulphate had been added, the mixture was further shaken for a few minutes and then warmed on the water-bath for 1 hour. *m*-Methoxybenzaldehyde formed was then separated in the usual manner. *m*-Methoxyphenylethylamine was then condensed with the acid chloride of phthalide-carboxylic acid exactly under the conditions described above for the amide (I). Phthalide-carboxy- β -m-methoxyphenylethylamide was thus obtained in almost quantitative yield. It crystallises in colourless plates, m. p. 105° . (Found: C, 69.6; H, 5.6. $C_{18}H_{17}O_4N$ requires C, 69.4; H, 5.5 per cent.).

3-Methoxyoxyprotoberberine, (IV).—The amide (III) (12 g.) was mixed with freshly distilled phosphorus oxychloride (120 c.c.), and the mixture heated for 6 hours on the water-bath. A copious evolution of hydrogen chloride was observed, the liquid gradually undergoing a change in colour through yellow to dark red. The mixture was decomposed by means of cold water and the liquid filtered, leaving a dark resinous residue. The yellow filtrate was then basified when an orange-red precipitate was obtained. This substance was collected, well washed with water, dried in the air, and boiled with zinc dust (25 g.) and glacial acetic acid (185 c.c.) for 5 minutes. Then more of zinc dust (25 g.) added and the whole mixture further boiled for $\frac{1}{2}$ hour. The cooled solution was diluted with a large amount of ethyl acetate, filtered and washed several times with dilute hydrochloric acid, then with aqueous sodium hydroxide and finally with water. The solution was dried over potassium carbonate and

the solvent removed by distillation. A yellow crystalline residue was left behind, which was repeatedly crystallised from alcohol, as beautiful needles, m. p. 148° , yield 2.5 g. (Found: C, 78.8; H, 5.5. $C_{18}H_{15}O_2N$ requires C, 78.0; H, 5.4 per cent.).

We wish to thank Dr. B.B. Dey of the Presidency College, Madras, for having kindly permitted the analyses required during investigation to be carried out in his laboratory.

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A Study of the Conductivity of Solutions of Zinc oxide in Caustic Soda Solution.

BY FREDERICK ROWLANDSON SNELL.

A study of the conductivity of solutions of alumina in caustic soda solution by Mata Prasad, Mehta, and Joshi (*J. Indian Chem. Soc.*, 1930, 7, 973) has suggested the existence in these solutions of sodium aluminate complexes with a lower ratio of $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O}$ than any of the well established sodium aluminates. In the present work an attempt has been made to see whether similar evidence is forthcoming in the case of solutions of zinc oxide in caustic soda solutions.

The literature dealing with the study of the constitution of solutions of zinc oxide in sodium hydroxide can be conveniently classified under three headings:—

- (a) Study of the phase rule equilibria (solubility etc.),
- (b) Study of hydrogen Ion concentration by *e.m.f.* measurement.
- (c) Study of conductivity.

(a) The greater part of the published work on solutions of ZnO in NaOH solution falls under this head. A large variety of solid phases have been reported, and much of the disagreement in the results of the different workers is no doubt due to indeterminacy of the solid phase. The most important references are those of Muller and Fauvel (*Z. Elektro Chem.*, 1924, 33, 140), Fricke (*Z. anorg. Chem.*, 1924, 136, 321, 344) and Goudriaan (*Rec. trav. Chim.*, 1920, 39, 505). Other references are Robenbauer (*Z. anorg. Chem.*, 1902, 30, 331), Klein (*ibid.*, 1912, 74, 157), Gutbier (*ibid.*, 1924, 176, 363), Dietrich and Johnston (*J. Amer. Chem. Soc.*, 1927, 49, 1419) and Forster and Gunther (*Z. Elektro Chem.*, 1899, 6, 301), (b) Britton (*J. Chem. Soc.*, 1925, 127, 2120) used the hydrogen electrode to follow the changes in p_{H} during the titration of Zn^{++} solutions with alkali. He found no inflections in the curve corresponding either to NaHZnO_2 (here contradicting Hildebrand's earlier work—*J. Amer. Chem. Soc.*, 1916, 38, 785) or to Na_2ZnO_2 .

(c) Certain conductivity measurements were made by Hantzsch (*Z. anorg. Chem.*, 1902, 30, 289) in order to ascertain the existence of colloidal Zn(OH)_2 in zincate solutions. He concluded that the colloidal form is present to a great extent, but he is ruthlessly criticised by Klein (*loc. cit.*). Certain *e.m.f.* measurements done

in 1927 by Dietrich also indicate that practically all the zincate in the solution is in the ionic form. Dietz, Dans and Tower (*J. Phys. Chem.*, 1929, 33, 605) however succeeded in preparing colloidal solutions of $\text{Zn}(\text{OH})_2$.

This survey indicates that the only complexes for which there is any considerable amount of evidence are those in which the ratio $\text{ZnO} : \text{Na}_2\text{O}$ is either 2:1 or 1:1 ($n=2$ or $n=1$). But since in the case of the aluminates Mata Prasad (*loc. cit.*) found discontinuities in the ratio-conductivity curves at the values 2:3, 1:2, 2:5, 1:3, 1:4, for the ratio $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O}$, it seemed worth while to examine the ratio-conductivity curves in the case of ZnO for similar evidence, although it is not possible to prepare solutions of ZnO in NaOH solutions having a value for 'n' of even as high as 0.5.

In the present work therefore an attempt has been made to gain information regarding the existence of complexes in strongly alkaline solutions by following the method used by Harman (*J. Phys. Chem.*, 1925, 29, 1155) for sodium silicate, and by Mata Prasad for sodium aluminate. Their method consisted in obtaining the conductivity ratio (ratio of SiO_2 or Al_2O_3 to Na_2O) curve. But the points on this curve were not obtained directly but indirectly from the measured conductivity-dilution curves at various ratios. This indirectness of their method has serious disadvantages in such strongly alkaline solutions in which impurities are very difficult to avoid. In the present work therefore the conductivity-ratio curves are directly determined.

EXPERIMENTAL.

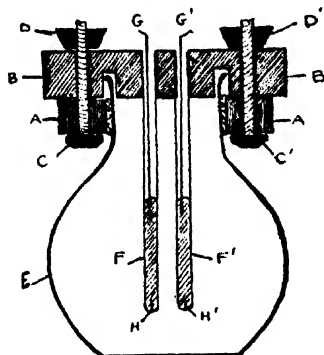
In the present experiments the strongest solution of ZnO in NaOH solution obtainable was placed in the conductivity cell, and a solution of NaOH of the same normality (with respect to NaOH) was added from a burette, the change of conductivity being measured meanwhile. The solution being very concentrated and the conductivity therefore high, a special form of cell was designed and made. This is shown in Fig. 1. The electrodes are formed by platinum wires fused through the ends of the glass tubes FF' (Fig. 1), ground flush with the glass and then covered with platinum black in the usual way. These tubes are supported rigidly by the wooden block B which is screwed down to a collar A, clamped round the neck of the flask in such a way that the position of the electrodes in the flask is rigidly determined. With a cell of this design the correction

of the cell constant for the variation in the volume of liquid in the flask was reduced to very small dimensions. The resistance of the solutions was measured in the ordinary way with a Wheatstone bridge circuit, using a buzzer and telephones. The estimated accuracy of the measurement of conductivity is about $\pm 1\%$.

The analyses of the solutions gave some difficulty at first. It was found, however, that the NaOH can be accurately titrated in presence of ZnO by using the indicator Brilliant Cresyl Blue. This method would not be applicable in dilute solutions. The ZnO in solution was determined by titration with $K_4Fe(CN)_6$ solution, using diphenylamine as an indicator (*J. Amer. Chem. Soc.*, 1927, **49**, 356). This titration was found extremely satisfactory. The cell flask was of Monax glass, but all other glass vessels used in making up the solutions were of Kavalier glass since this contains a larger proportion of alkaline oxides, and may therefore be expected to be more resistant to the strongly alkaline solutions used. Kavalier glass has also the advantage of being free from Zn and Al.

The NaOH used was Merck's pure sticks. These were dissolved in about an equal weight of water, keeping the solution cool, to give a solution of about 16N. This was then allowed to stand

Fig. 1.



- A. Annular split collar with cork washer clamped rigidly by means of two screws (not shown) round the neck of the 150 c.c. Monax Flask E.
- B. Wooden block carrying electrode tubes FF' and terminals (not shown) to which the lead wires GG' are connected. There is also a third hole (not shown) through the block by which the nozzle of the burette is introduced.
- CD and C'D'. Brass bolts and nuts by means of which B can be screwed firmly down onto A.
- HH', Platinum wires, fused through the ends of the tubes FF', ground flush with the glass, and blacked with platinum.

for several days, until all solid matter (Na_2CO_3 , etc.) had settled. It was then carefully siphoned off and diluted for use as required. This procedure avoids the highly undesirable filtration through glass-wool. The ZnO used was Merck's 'Pure', which analysis showed to be 99.5% ZnO . It was found necessary to boil the ZnO with the NaOH solution in order to get it to dissolve. With 14 N alkali, indicated by Muller's curves as the best to use, the maximum ratio of $\text{ZnO}:\text{Na}_2\text{O}$ obtainable was found to be about 0.400. This solution was allowed to settle and the clear liquid diluted for use as required. A check made with alkali only, boiling for a similar length of time and under similar conditions showed no appreciable change of conductivity due to the heating.

In each experiment 50 C.c. of the ZnO solution were placed in the cell and the conductivity measured. Alkali of the same normality (as calculated from the titration with 1.0N acid with Brilliant Cresyl Blue as Indicator) was then added from a burette, and the conductivity determined at intervals. If 'v' was the volume added, and n_0 the initial $\text{ZnO}:\text{Na}_2\text{O}$ ratio as determined by analysis, n_v was calculated from the formula: $-n_v = n_0 \times (50/50 + v)$. Check analyses at the end of each experiment showed that this method of calculation (neglecting possible volume changes) was satisfactory. Particularly in the more concentrated, and therefore more viscous, solutions, time had to be allowed for equilibrium to be reached, but if the solution was frequently shaken, 30-40 minutes were found to be sufficient for this. The ZnO solutions were kept for at least a week after being made up before they were used. All experiments were carried out in an electrically regulated thermostat at 25.0° with a maximum temperature variation of $\pm 0.03^\circ$.

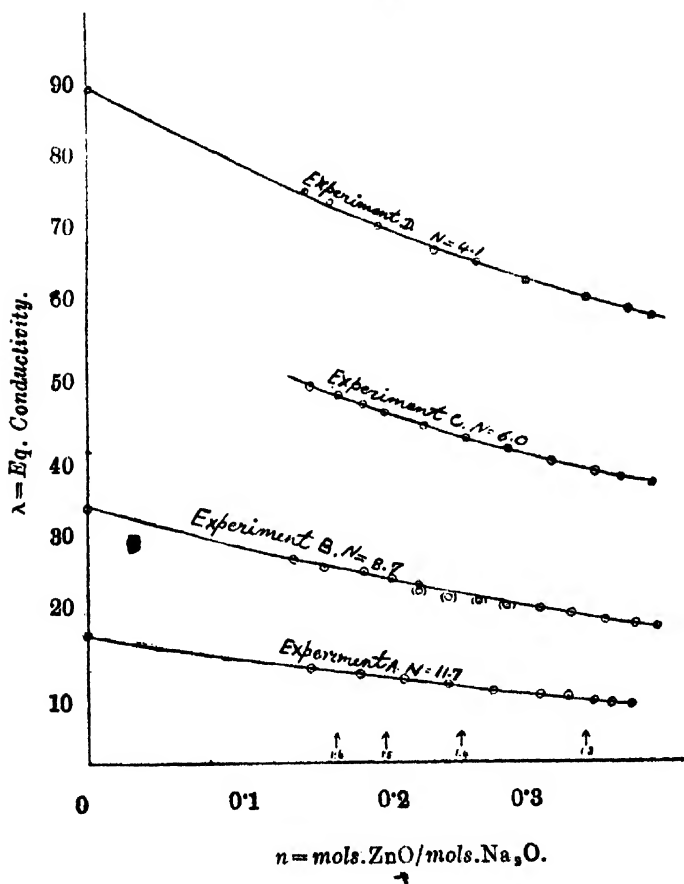
At the beginning and end of each experiment the electrodes were transferred to KCl solution to verify that no change had taken place in the cell-constant, due to action of the solution on the electrodes. The cell-constant was determined with 0.1N KCl solution.

Results.

The results are given in Table I, and plotted in Fig. 2. 'n' is the ratio of mols. ZnO to mols. Na_2O ; λ is the equivalent conductivity with respect to normality of NaOH , calculated from $\lambda = \frac{10^3 \cdot K}{NR}$, where K is the cell-constant; R the observed resistance, and N the

normality with respect to NaOH. The curves are nearly linear, but show a slight concavity towards the 'n' axis. There is, however, no evidence of any discontinuities in any of them over the range covered. The four points from Experiment B, which are shown in Fig. 2 in brackets, are of some interest in connection with the time lag. In determining all other points in Experiment B, a time of not less than 40 minutes was allowed to elapse after addition of the alkali. But in the case of the four points mentioned, the time intervals were only 15, 15, 7, 7, minutes respectively.

Fig. 2.



Determination of Flocculation Values from Measurements of the Rate of Coagulation of an Arsenic Sulphide Sol.

BY D. N. GHOSH.

Numerous investigators have determined flocculation values from measurements of the time required for the production of a certain state of turbidity of the sol. Flocculation values thus determined are not strictly comparable as they refer to a transitory state during the process of coagulation. It is much more important to measure the velocity of coagulation as coagulation is really a process of the progressive growth of particles. Before a change in a physical property of a sol, *e.g.*, of turbidity, change in viscosity etc., can be made the basis for the determination of flocculation values, it must be clearly shown that the rate of flocculation goes parallel with changes in the physical property chosen. Gann (*Koll. Chem Beih.*, 1916, 8, 64) attempted to study the rate of coagulation of aluminium hydroxide sol by measuring the rate of change of viscosity, but his measurements are doubtful as the assumption that the rate of change of viscosity is proportional to the velocity of coagulation is not strictly valid. In the present paper an attempt has been made to determine flocculation values from measurements of the velocity or the rate of increase of turbidity of arsenious sulphide sol with different electrolytes.

During the measurements a Nutting colorimeter was adapted to

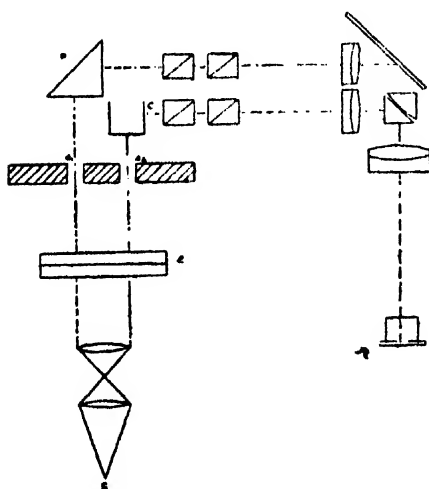


FIG. 1.

function as a tyndallmeter. A 130 C.P. point-o-lite lamp is placed at S (Fig. 1). By means of a system of lenses the light was rendered parallel and was then passed through a Zeiss monochromatic filter L, which transmitted 80 per cent. of the Hg green line 5461. By means of two slits s_1 and s_2 part of the parallel beam was allowed to pass through the rectangular cell C, containing the sol-electrolyte mixture, whereas another part

was allowed to fall on a right angled prism and was totally reflected.

The intensity of the scattered beam was compared with the intensity of the beam directly reflected from the right angled prism by means of the tyndallmeter. A sample of arsenious sulphide sol was prepared by the usual method and different volumes of electrolytes were added to 1 c.c. of the sol, the total volume being made up to 4 c.c. in every case. The sol-electrolyte mixture was immediately transferred to the cell and the change in the intensity of the scattered beam with time was followed on the tyndallmeter. To eliminate the disturbing effects of the stablising ions the electrolytes chosen were such that the negative ion was the same throughout.

Mecklenberg (*Kolloid Z.*, 1915, 16, 97), using Odén's sulphur sol has shown that the intensity of the scattered beam is proportional to the size of the particles of diameters between the limits $5.95\mu\mu$. Bechold and Hebler (*ibid.*, 1932, 31, 70) using barium sulphate suspensions has shown that the above relationship is valid for particles of size up to $800\mu\mu$. In the present experiments the observations are mainly confined to the earlier stages of the process. Consequently it seems reasonable to assume that the rate of change of the intensity of the scattered beam is proportional to the rate of growth of the particles. The experimental data obtained are given in the following table.

TABLE I.

Electrolyte—HCl.

Expt. No.	Electrolyte conc. millimol/litre	Time		Rate of Coagulation.		
		min.	sec.	Scale reading.	0 tan θ	
I	31 26	0	18	0		
		6	0	0 1	1	02
		14	30	0 2		
II	45	2	21	0 5		
		3	56	1 3	5	08
		5	27	1 6		

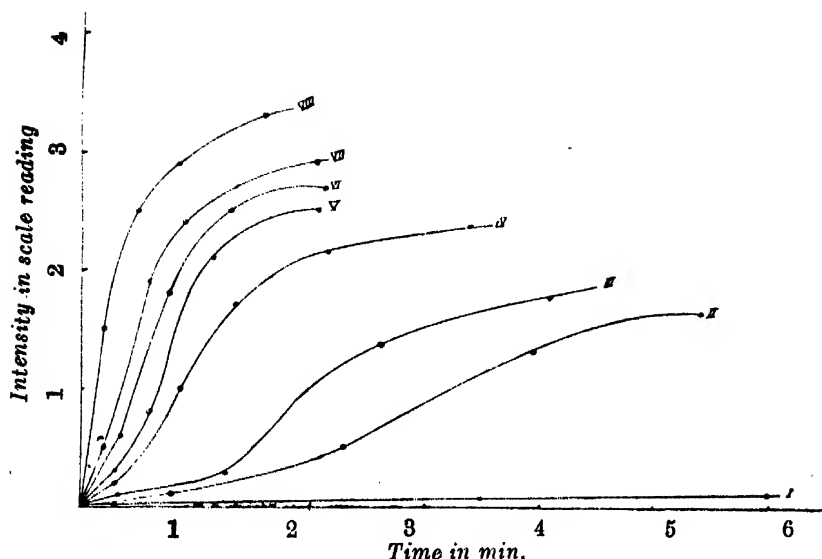
TABLE I.—contd.

Electrolyte—HCl.

Expt. No.	Electrolyte conc. millimol./litre	Time		Rate of coagulation.		
		min.	sec.	Scale reading.	0	tan θ
III	50	0	8	0 1		
		1	15	0 3		
		2	21	1 3	12	21
		4	6	1 8		
		5	6	2 0		
IV	56 2	0	18	0 2		
		0	51	1 0		
		1	21	1 7		
		2	9	2 1	31	60
		3	24	2 4		
		5	30	2 6		
V	59 37	0	18	0 3		
		0	36	0 6	45	1 0
		1	9	2 1		
		2	3	2 5		
VI	62 5	0	21	0 6		
		0	45	1 8	56	1 48
		1	18	2 5		
VII	65 62	0	12	0 5		
		0	21	1 9	66	2 24
		0	54	2 4		
		2	3	2 9		
VIII	71 94	0	18	1 5		
		0	30	2 5	81	6 3
		0	51	2 9		
		1	21	3 3		

Electrolyte—HCl.

FIG. 2.



The scale readings shown in the table represent the intensities of the scattered beams. The scale readings have been plotted against time and a series of curves have been obtained. The curve for hydrochloric acid is shown in Fig. 2 which is generally typical of the curves obtained with other monovalent electrolytes. Corresponding to hydrochloric acid concentration equal to 45 and 50 millimols per litre the curve assumes the characteristic shape of the curves for autocatalytic reactions. Similar behaviour was observed for all monovalent electrolytes. $\frac{dI}{dt}$, the rate of change of the intensity of the scattered beam with time, has been obtained in the case of each electrolyte from the above curves by the graphical method. θ , the angle between the tangent to the curve at any point and the abscissæ was read directly when the value of $\frac{dI}{dt}$ for that point was known, being equal to $\tan \theta$. The values of $\frac{dI}{dt}$ so obtained were plotted against concentration and the series of curves as shown in Figs. 3 and 4 were obtained.

FIG. 3.

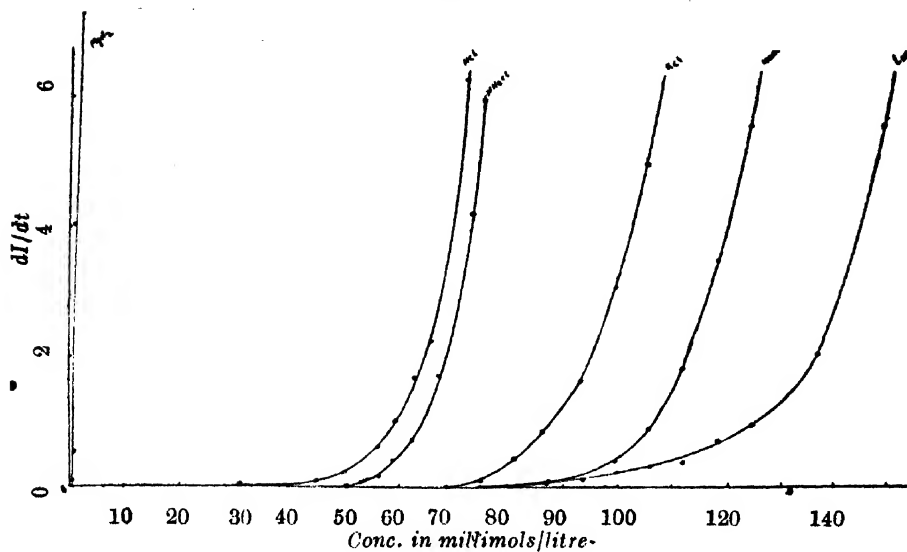
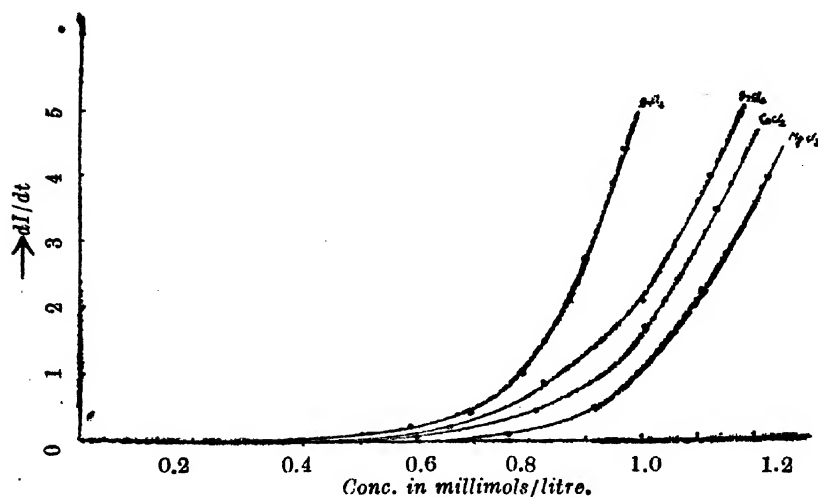


FIG. 4.



From a study of the curves (Fig. 3 and 4) which shows the variation of the rate of coagulation with change in electrolyte concentration, the flocculation values of the different electrolytes can be obtained. The values of C for different electrolytes at any fixed value of $\frac{dI}{dt}$ give the flocculation values. From the experimental

results it has been found that the flocculation values in the case of monovalent electrolytes are in the following order :—

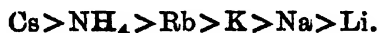


whereas in the case of the divalent electrolytes the order is :—

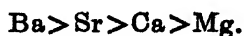


The important factors during a coagulation process are the neutralisation of the charge on the particle generally by the adsorption of an oppositely charged ion and the later adsorption of one or both the ions of the coagulator by the electrically neutral aggregates formed by coalescence of discharged particles. It is evident that the difference in the orders of flocculation values obtained by different authors is caused to a large extent by the disturbances due to adsorption by flocculated aggregates. To guard against this effect in the present experiments observations have been limited to the earlier stages of coagulation.

Oden (*J. Phys. Chem.*, 1921, 25, 311) studied the relative adsorbability of the ions using blood charcoal as the adsorbent, and in the case of the alkali metals he obtained the series :—



With the alkaline earth metals he obtained the series :—



Weiser (*J. Phys. Chem.*, 1921, 25, 399) using arsenious sulphide precipitate as the adsorbent has also obtained the same order for both mono- and divalent ions. Since coagulation values can be taken as the inverse of adsorption values, it is interesting to note that the order of flocculation values as obtained during the present investigation is the reverse of the order for the adsorption as obtained by Oden. The present experimental arrangement thus appears to be well suited for reliable measurements of flocculation values.

Westgren (*Arkiv. kemi., Stockholm*, 1918, 7, No. 6,1) studied the slow coagulation of gold sol and from his measurements it was concluded that the order of the flocculation values changed with concentration of the coagulator. The adsorption isotherms as found by Oden (*loc. cit.*) however, do not support the above conclusion. From the present experiments it is evident that the order of flocculation

values is fixed for all different concentrations of electrolytes. Where discrepancies have been observed, they are due largely to defects in the experimental methods of determining flocculation values.

In conclusion I wish to express my thanks to Dr. P. B. Ganguly for his kind interest in the work.

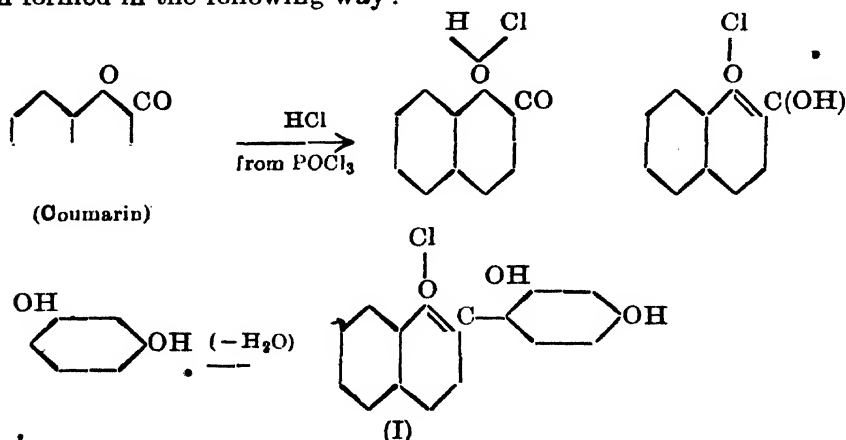
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A Preliminary Note on a New Method of Synthesising Benzopyrylium Compounds.

By M. N. GOSWAMI AND AMIYA KUMAR CHAKRAVARTI.

While studying some reactions of coumarin, the authors had come across a remarkable reaction between it and resorcin in presence of phosphorus oxychloride. A mixture of coumarin (8 g.), resorcin (6 g.) and phosphorus oxychloride (5 c. c.) was heated with an air condenser on the water-bath until the red solution so formed became thick. On cooling and being treated with ice-cold dry ether (in which both coumarin and resorcin are freely soluble) an orange-red compound was precipitated. On washing with dry ether it was obtained as brilliant scales from alcohol, m. p. 185° (decomp.). It is insoluble in ether, carbon disulphide and other common organic solvents except alcohol. It is appreciably soluble in water. It dissolves in alkali to a reddish brown solution, the colour of which is discharged by acid. It contains chlorine and is highly hygroscopic. The compound was kept for about six months in a vacuum desiccator and on analysis it was found to contain C, 54.5; H, 5.72;* whilst $C_{15}H_{11}O_3Cl \cdot 3H_2O$ requires C, 51.79; H, 5.14 per cent. The behaviour of the compound is similar to that of benzopyrylium salt and it was thought that the compound had the following structure (I) and it had been formed in the following way :

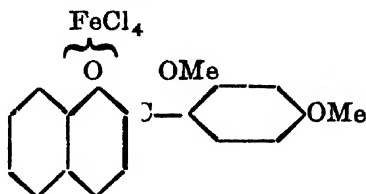


* The extreme hygroscopic nature of the compound causes great difficulty in its analysis and this is responsible for the high value of hydrogen. This difficulty has been experienced with pyrylium compounds by many other workers.

If this representation is correct then the compound is 2':4'-dihydroxy-2-phenylbenzopyrylium chloride. On reference to the literature it was found that this compound had not yet been synthesised.

An attempt was then made to synthesise the compound after the method of Robinson and Robertson (*J. Chem. Soc.*, 1926, 1951) from salicylaldehyde and resacetophenone. It was found that although the intermediate styryl compound was easily obtained, the final stage to close up the ring always led to the formation of tarry matter. The attempt in this direction having proved abortive, the dimethoxy derivative of the original compound was prepared by taking dimethoxyresorcin, coumarin and phosphorus oxychloride. It gave a ferrichloride as orange-red needle shaped crystals, m. p. 175° (A). (Found: Cl, 30.58; Fe, 11.85. $C_{17}H_{15}O_3$, $FeCl_4$ requires Cl, 30.54; Fe, 12.04 per cent.).

This dimethoxy derivative was, however, successfully prepared by the ordinary synthetic method, *via* salicylaldehyde and dimethoxyresacetophenone. It was obtained (B) as orange-red needle shaped crystals, m. p. 175° . (Found: Cl, 30.52; Fe, 12.06. $C_{17}H_{15}O_3$, $FeCl_4$ requires Cl, 30.54; Fe, 12.04 per cent.). Mixed melting point of (A) and (B) was also found to be 175° . The compound (A) is therefore identical with compound (B) both of which have the following structure as proved by synthesis.



This compound, too, has not been synthesised as yet.

Almost all other phenols and phenolic ethers have been found to condense similarly with coumarin and substituted coumarins in presence of phosphorus oxychloride to give benzopyrylium compounds and they will be published in a future communication. The method gives a new and an easy way to prepare various types of benzopyrylium salts and undoubtedly opens a vast field of possibilities which the authors desire to explore.

The Fluoremetric Formula.

BY K. S. GURURAJA DOSS,

Desha (*J. Amer. Chem. Soc.*, 1920, **42**, 1363) has described a new method of analysis of the same order of sensitiveness as colorimetry and nephelometry. He has called it fluoremetry, the property of fluorescence being taken advantage of in the process. This technique will certainly prove highly useful for the determination of minute quantities of a considerable number of substances which are either fluorescent by themselves or can be rendered so by means of suitable reagents.

In his experiments, ultra-violet rays from a mercury arc filtered from most of the visible radiation are used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kober-nephelometer. The intensity of fluorescent light thus produced, as observed in the eyepiece of the instrument, is equalised in the usual manner by altering the heights of the columns included in the field of view of the optical plunger.

He finds that for sufficiently dilute solutions the curve obtained by plotting the scale readings against concentration is quite regular. He also says that such a curve corresponds more closely to the curve drawn according to the Kober's nephelometric formula than that of inverse proportionality (colorimetric curve). He also suggests that a further elimination of the errors in the measurement or a further modification of the formula may reduce the lack of agreement.

The Kober's nephelometric formula referred to in the above paper is empirical as is evident from Kober's own words (*J. Biol. Chem.*, 1913, **13**, 408): "The readings of the nephelometer plotted against the ratios of solutions for a given standard solution and a given height of the standard, seem to follow a uniform curve which can be expressed in the equation $y = \frac{S}{x} - \frac{S(1-x)k}{x^2}$, where y is the height of the un-

known solution, S , the height of the standard solution, and x , the ratio of solutions. An attempt is made by Wells (*J. Amer. Chem. Soc.*, 1922, **44**, 267) to give a theoretical basis for the Kober's formula; but his theoretical first approximation formula proves to be simpler than Kober's, and the latter is in better agreement with experiment; as Wells himself points out, this reflects on the unknown factors introduced in nephelometry. In the possibly simpler case of fluoremetry it may be advantageous to derive a theoretical formula and compare it with Kober's, an attempt at which is made in this paper.

Studies on the intensity of fluorescence show that traces of an active substance present in a medium are capable of producing intense fluorescence and if the concentration is increased beyond a few per cent., the brightness is greatly reduced. The existence of the optimum concentration has been explained by Brunninghaus (*Compt. Rend.*, 1909, **149**, 1375) as a result of absorption of light; the increase in concentration though brings about an increase in fluorescence there will be an increase in absorption and the fluorescent intensity is therefore given by an equation of the form $I = Kxe^{-kx}$, where x is the concentration of the fluorescent substance. Though this was in accordance with the measurements made on the cathodo-luminescence of manganese in calcium phosphate it is unable to explain recent experimental work (Merritt, *J. Opt. Soc. Amer.*, 1926, **12**, 613), Perrin (*Compt. rend.*, 1924, **178**, 1405) has tried to explain the same phenomenon on the basis of protective action. Perrin's idea has been successfully made use of by Merritt (*loc. cit.*) to explain quantitatively the variation of fluorescent power with concentration. Recently, Jette and West (*Proc. Roy. Soc.*, 1928, **A**, 121 299) have suggested an explanation by extending the conception of the collisions of the second kind to the case of solutions. They ascribe the diminishing fluorescent power of a substance with increasing concentration to the collisions of the second kind between the photo-excited and the ordinary fluorescent molecules. It is also to be noted that a "Perrin protection" becomes more or less identical with a collision of the second kind if the former is assumed to take place only at molecular distances. If the life of the excited molecule is long enough, the intensity may also depend on the viscosity of the solution which affects the rate of diffusion and hence the probability of the molecule being within the range of action of another fluorescent molecule, in the duration of

the excited state. The duration of the excited state is found to be very brief in the case of aqueous solutions (Perrin: *Compt. rend.*, 1926, 182, 219).

Let us now apply the above ideas for the derivation of the formula for fluoremetry. Let us assume that if two fluorescent molecules are at a distance apart that is less than a distance ρ , their luminiscence is completely destroyed or greatly reduced. In the case of aqueous solutions where the duration of the critical state is small, if we direct our attention on some molecule, the probability that another molecule will not lie within a sphere of radius ρ is $1 - \frac{4\pi\rho^3}{V}$. The probability that all of the other molecules

satisfy the condition is $\left(1 - \frac{4\pi\rho^3}{V}\right)^n$, where n is the number of molecules in V c.c.

If we put $V=1$, and $n = \frac{cN}{M}$, where c is the concentration in grammes per c.c., M the molecular weight, N the Avogadro number, then the probability expression reduces itself to $e^{-\gamma c}$, where $\gamma =$

$$-\log e \left(1 - \frac{4\pi\rho^3}{V}\right)^{N/M}$$

Now as c is the total concentration, the effective concentration of the fluorescent molecules is $c e^{-\gamma c}$.

Let us consider a layer of solution of thickness dy . Let the distance through which the normally incident light must travel through the solution before it can reach the axis of the plunger be Δ . Let the incident intensity be I_0 . Then the intensity of the light exciting the molecule under the field of view of the plunger is $I_0 e^{-(a+bc)\Delta}$, where a and b are the absorption coefficients for the solvent and the solute respectively for the incident radiation. (We assume here the truth of Lambert and Beer's law for fluorescent substances: cf. Kempf, *Physikal. Z.*, 1911, 12, 761; Nichols and Merritt, *Phys. Rev.*, 1910, 31, 500).

Then the fluorescent intensity due to the layer will be

$$\lambda I_0 e^{-(a+bc)\Delta} c e^{-\gamma c} dy$$

where λ is a constant. Applying correction for the absorption of fluorescent light by successive layers we get, the fluorescent intensity due to the layer

$$dI = \lambda I_0 e^{-(a+bc)\Delta} c e^{-\gamma c} e^{-(p+qc)y} dy$$

where p and q are the absorption coefficients for the solvent and solute respectively for the fluorescent radiation. By integration we get the expression for the total intensity which is kept constant in any single set of fluoremetric measurements. So, one may write

$$c e^{-\gamma c} e^{-(a+bc)\Delta} \frac{\left\{ e^{-(p+qc)h} - 1 \right\}}{-(p+qc)} = \text{constant.}$$

This is the accurate formula for fluoremetry.

But this formula is too complicated for actual use in practice. So let us carry out a few approximations. If we assume that the correction for absorption is small (which is satisfied by dilute solutions) we can use the well-known approximation formula

" $e^x - 1 = xe^{x/2}$ ", and express the above relation in the form

$$ch e^{-\beta c} \cdot e^{-\frac{(p+qc)h}{2}} = K_1$$

where β and K_1 are constants. This formula can be directly employed as p and q can be directly measured and the other two constants can be calculated from two measurements of c and h . To simplify the expression further, we can carry out the following approximation:

We can neglect $\frac{ph}{2}$, as the amount of light absorbed by water is small and assume that $\frac{qch}{2}$ is constant in the correction factor as ch is fairly constant owing to the smallness of the absorptive and protective effects. Then we get

$$ch e^{-\beta c} = K_2$$

Let us now study the relationship of this formula to the usual empirical formulæ used in nephelometry.

As the absorption and protection effects are of a small order we can put $c = \frac{k}{h}$ in the correction factor. Thus we get

$$ch e^{-ak/h} = \text{constant.}$$

Or we can write

$$c_1 h_1 e^{-ak/h} = c_2 h_2 e^{-ak/h}$$

or

$$\frac{c_1}{c_2} = \frac{h_2}{h_1} \left\{ 1 + ak \left(\frac{1}{h_1} - \frac{1}{h_2} \right) \right\}$$

to a first approximation. If h_2 is the standard height we can put $\frac{ak}{h_2} = -\delta$ and hence,

$$\frac{c_1}{c_2} = \frac{h_2}{h_1} \left\{ 1 + \delta \left(1 - \frac{h_2}{h_1} \right) \right\}.$$

This formula is identical with Wells' empirical formulæ for nephelometry, which has been tested and found to be in agreement with Kober's data (Wells; *loc. cit.*). This is more convenient for use especially for the slide rule. Also it is to be pointed out that it is so closely approximated a form of the original formula that we get values never differing by more than 0.1% when calculated on the basis of either formulæ.

Now let us proceed in another direction. Again,

$$c_1 h_1 c^{-\beta c_1} = c_2 h_2 c^{-\beta c_2}.$$

$$\frac{h_1}{h_2} = \frac{c_2}{c_1} \left\{ 1 + \beta c_1 \left(1 - \frac{c_2}{c_1} \right) \right\}$$

to a first approximation. This is of the same form as the Kober's formula:

$$\frac{h_1}{h_2} = \frac{c_2}{c_1} \left\{ 1 + k \left(1 - \frac{c_2}{c_1} \right) \right\}$$

and the two can be equated if c_1 is constant, i.e., if it is the concentration of the standard solution. But Kober takes c_2 as the standard and so far the theoretical formula differs from Kober's.

FIG. 1.

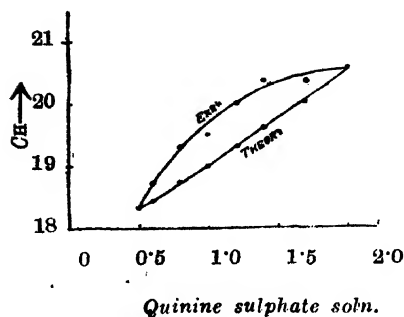
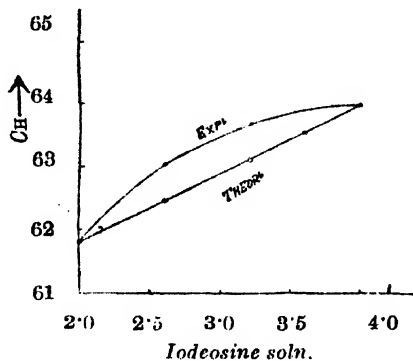


FIG. 2.



Let us now consider the available experimental data. Apart from the indirect support offered by the Kober's nephelometric data, the theoretical formula in the Wells form seems to be in fair agreement with Desha's fluoremetric data on iodeosine solutions, the maximum difference between theory and experiment being about 1% (see Table II and Fig. 2). But the data on quinine sulphate solutions show a large deviation, the maximum amounting to about 4% (See Table I and Fig. 1).

Lastly let us examine the shape of the " $ch-c$ " curve as obtained from Desha's experimental data. As c is a continuous function of h , we must expect the " $ch-c$ " curve to be continuous. The mean smooth experimental curve is found to be convex towards the Y-axis. This is an extremely interesting observation if we could absolutely depend on Desha's results. For, whereas the accurate theoretical formula must give a curve concave to the Y-axis even at fairly high concentrations, we find just the reverse to be the case in practice. This discrepancy between the theoretical and the experimental values seems to be of profound significance from the point of view of the theory of fluorescence in general and the theories of inhibition of fluorescence in particular. I would not like to attempt at any quantitative derivation to account for the difference, as I feel that some more experimental work is necessary to consider this as but a sure and general tendency.

TABLE I.

Quinine sulphate solutions.

<i>c.</i>	<i>h</i> (exp.).	<i>h</i> (theor.).	<i>ch</i> (exp.).	<i>ch</i> (theor.).
2.0	10.28	10.28	20.56	20.56
1.7	11.98	11.80	20.37	20.06
1.4	14.53	14.00	20.34	19.60
1.2	16.76	16.08	20.11	19.80
1.0	19.50	19.00	19.50	19.00
0.8	24.10	23.40	19.28	18.72
0.6	31.15	30.73	18.69	18.44
0.5	36.60	36.60	18.30	18.30

TABLE II.

Iodeosine solutions.

<i>c.</i>	<i>h</i> (exp.).	<i>h</i> (theor.).	<i>ch</i> (exp.).	<i>ch</i> (theor.).
4.0	16.00	16.00	64.00	64.00
3.6	17.83	17.65	64.19	63.54
3.2	19.90	19.72	63.68	63.10
2.6	24.25	24.02	63.05	62.45
2.0	30.90	30.90	61.80	61.80

In conclusion I thank Professor J. N. Mukherjee, D.Sc. for his valuable suggestions and criticism.

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Effect of Sugars on the Inhibition of the Precipitation of Ceric Hydroxide from a Solution of Ceric Ammonium Nitrate.

BY M. V. NABAR AND MATA PRASAD.

Dhar (*Kolloid Z.*, 1923, **33**, 193), Mehrotra and Sen (*J. Indian Chem. Soc.*, 1927, **4**, 117), and Sen (*J. Indian Chem. Soc.*, 1927, **4**, 131), have studied the peptisation of various metallic hydroxides in the presence of sugars. They have determined the amount of sugar which is necessary to prevent the precipitation of the hydroxides by alkali. Patel and Desai (*J. Indian Chem. Soc.*, 1930, **7**, 161), have studied the effect of non-electrolytes on the precipitation of thorium hydroxide from a solution of thorium nitrate by alkali. They find that sugars and glycerol alone are effective in preventing or inhibiting the precipitation. Nabar, Patel and Desai (*Kolloid Z.*, 1931, **57**, 173), find that the inhibition of the precipitation of thorium hydroxide increases with an increase in the hydroxyl groups in sugars.

The present investigation deals with the study of the effect of non-electrolytes on the inhibition of the precipitation of ceric hydroxide from a solution of ceric ammonium nitrate from the viewpoint put forward by Nabar, Patel and Desai (*loc. cit.*). The peptisation of ceric hydroxide from ceric chloride by sugars has already been studied by Mehrotra and Sen (*loc. cit.*). •

EXPERIMENTAL.

An approximately $M/40$ solution of ceric ammonium nitrate (B. D. H.) was prepared and its concentration was accurately determined. A solution of Merck's extra pure caustic soda was prepared, standardised and stocked in a Jena-glass flask. The non-electrolytes used were, (1) ethylene glycol, (2) glycerol, (3) mannitol, (4) glucose, (5) lactose, (6) maltose, (7) sucrose, and (8) fructose. •

A known volume of ceric ammonium nitrate was taken in a number of test tubes and the total volume was made up to 30 c.c. by adding different amounts of non-electrolytes and distilled water. 5 C.c.

of sodium hydroxide solution was taken in another set of test tubes ; the amount of NaOH in 5 c.c. was more than that required for the complete precipitation of cerium nitrate contained in the former set of test tubes. The contents of the two sets of tubes were then thoroughly mixed, the same mode of mixing being followed throughout the investigation. The amount of the non-electrolyte in the tube, in which the appearance of the precipitate is just prevented, is the minimum amount required to inhibit the precipitation of ceric hydroxide. Two series of such observations were taken and the mean of the two is given in all the following tables.

Effect of volume.—The effect of the change in the total volume of the mixture on the amount of sugars required to inhibit the precipitation of ceric hydroxide by a fixed amount of NaOH is given in Table I.

TABLE I.

NaOH in the mixture = 1.25 m. mols. Ceric ammonium nitrate = 0.05 m. mols.

Total volume.	Non-electrolytes required in m. mols.				
	Fructose.	Sucrose.	Maltose.	Lactose.	Glucose.
10 c. c.	0.98	0.064	0.225	0.525	2.15
20	0.064	0.058	0.156	0.406	1.5
30	0.048	0.054	0.119	0.35	1.25
40	0.048	0.054	0.119	0.35	1.25
50	0.048	0.054	0.119	0.35	1.25
60	0.048	0.054	0.119	0.35	1.25

It appears that with an increase in the total volume of the mixture, the amount of sugar required to inhibit the precipitation at first decreases and then reaches a constant value.

The clear liquid obtained in these mixtures was cataphoretically examined and was found to be a sol containing negatively charged particles. The formation of these particles is due to the adsorption of OH⁻ ions by ceric hydroxide in the presence of sugars which are also probably adsorbed to some extent by the colloidal particles. The decrease in the amount of sugars with an increase in the total volume is due to the stabilisation of the sol on dilution.

Effect of the amount of ceric ammonium nitrate.—The effect of the amount of the salt on the non-electrolytes required to inhibit the precipitation by a fixed amount of caustic soda (1.25 m. mols.) is given in Table II. The total volume of the mixture was 30 c.c.

TABLE II (A).

Ceric ammonium nitrate (in m. mols.).	Non-electrolytes required in m. mols..				
	Fructose.	Sucrose.	Maltose.	Lactose.	Glucose.
0.025	0.024	0.022	0.056	0.150	0.500
0.0375	0.034	0.038	0.088	0.250	0.800
0.05	0.048	0.054	0.119	0.350	1.250
0.0625	0.070	0.078	0.163	0.475	1.900
0.075	0.090	0.118	0.238	0.663	2.700
0.0875	0.130	0.150	0.338	—	4.100

TABLE II (B).

Ceric ammonium nitrate (in m. mols.).	...	0.0062	0.0125	0.0156	0.0187	0.025	0.0375
Mannitol (in m. mols.)	0.325	0.525	1.125
Glycerol	„	...	0.60	1.45	...	2.2	3.1
Ethylene glycol	„	2	3.3	4.8	6.8

The tables show that the amount of non-electrolytes required* is greater as the amount of salt in the mixture is increased. These results are similar to those obtained by Mehrotra and Sen (*loc. cit.*) in the peptisation of the ceric hydroxide. This increase in the amount of sugars is due to an increase in the number of colloidal particles of ceric hydroxide formed in a fixed volume of the mixture.

The inhibiting power of the non-electrolytes increases as, ethylene glycol < glycerol < mannitol < glucose < lactose < maltose < fructose < sucrose. This shows that the number of OH groups in the non-electrolyte influences its inhibiting power; cane sugar, maltose and lactose which contain eight OH groups are better inhibitors than glucose and fructose, glycerol and glycol which contain five, three and two OH groups respectively. The behaviour of fructose is anomalous as its

inhibiting power is more than that of sucrose which contains more OH groups than fructose. The ketone group in fructose may be responsible for this anomaly.

Effect of the amount of alkali.—The following table shows the effect of the addition of increasing amounts of alkali on the amount of the non-electrolyte required to inhibit the precipitation.

TABLE III.

Ceric ammonium nitrate = 0.025 m. mols. Total vol. = 30 c.c.

NaOH (in m. mols.).	Amount of non-electrolytes required in m. mols.					
	Fructose.	Sucrose.	Maltose.	Lactose.	Glucose.	Glycerol.
0.25	0.130	0.160	0.219	0.969	7.75	20.00
0.375	0.050	0.078	0.113	0.382	1.90	11.00
0.50	0.034	0.060	0.082	0.244	0.85	6.00
0.75	0.024	0.030	0.056	0.175	0.50	1.75
1.00	0.024	0.022	0.056	0.150	0.50	1.75
1.25	0.024	0.022	0.056	0.150	0.50	1.75

With an increase in the amount of alkali, the amount of non-electrolyte required to inhibit the precipitation at first decreases and then reaches a constant value.

Separate experiments showed that the non-electrolytes alone could not inhibit the precipitation of the hydroxide if the amount of the alkali added was not greater than that required for complete precipitation. The part played (by the excess of the hydroxyl ions) in the inhibition is indicated by the decrease in the amount of the non-electrolyte required to inhibit the precipitation and is due to the stabilising influence of these ions. But certain minimum amount of the non-electrolyte is also essential for causing the inhibition in precipitation; sodium hydroxide alone can not inhibit the formation of the precipitate. The decrease in the amount of the non-electrolytes required in the presence of increasing amount of NaOH may possibly be due to the suppression in the adsorption of the non-electrolyte by OH ions. Experiments on the adsorption of these non-electrolytes under conditions described above are necessary before any definite conclusion regarding the inhibition of the precipitation can be drawn.

Summary.

The effect of (1) change in total volume, (2) amount of salt and (3) amount of alkali on the inhibition of the precipitation of ceric hydroxide from ceric ammonium nitrate solution by non-electrolytes has been studied.

The amount of the non-electrolyte required for inhibiting the precipitation decreases with an increase in (1) the total volume, and (2) the amount of alkali in the mixture up to a certain limit and then reaches a constant value but it increases with an increase in the amount of cerium ions in the solution. •

The inhibiting power of the non-electrolytes decreases as sucrose > fructose > maltose > lactose > glucose > mannitol > glycerol > glycol.

The effect of the excess of alkali and of the non-electrolytes on the inhibition of the precipitation is discussed.

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A Comparative Study of Jute and Cotton Celluloses.

By J. K. CHOWDHURY AND N. N. BASU.

The complex problem of the identity of celluloses from different sources has received attention from several investigators. Cross and Bevan and other investigators (Kruger, *Papier Fabr.*, 1925, **23**, 767) believed that each variety of cellulose is different from the other and speak of celluloses and not of cellulose as a chemical unit. If this view be correct, each kind of cellulose would have a different chemical constitution and it would obviously be impossible to assign a definite chemical formula to cellulose.

Another school of investigators represented mainly by Heuser and his co-workers (Heuser and Haug, *Z. angew. Chem.*, 1918, **31**, 99; Heuser and Boedeker, *ibid.*, 1921, **34**, 461; Heuser and Aiyer, *ibid.*, 1924, **37**, 27) maintain that cellulose is a definite chemical entity. According to this view it would not only be possible to employ a general constitutional formula for all kinds of cellulose but it would also be possible to use cheaper varieties as raw material for the manufacture of different cellulose derivatives and for other cellulose industries. The question of the identity of celluloses is therefore important both from the theoretical and the industrial point of view.

The object of this investigation is to examine these two points of view, taking jute and cotton celluloses as a basis for comparison. For this purpose it is first necessary to prepare a standard cellulose from cotton and to purify jute cellulose in such a manner that it may approximate the standard cotton cellulose in its properties. The properties of the two standard celluloses can then be compared under identical conditions, special attention being given to the following:

- (1) Acetylation of the celluloses.
- (2) Yield of glucose. (a) As methylglucoside (Irvine and Hirst),
(b) as crystalline glucose (Monier Williams).
- (3) Yield of cellobiose octa-acetate.
- (4) Methylation of cellulose.
- (5) Characterisation of the cellulose by means of viscose reaction.

- (6) Surface tension of viscose solutions.
- (7) (a) Viscosity of the celluloses in cupra-ammonium solution,
(b) viscosity of cellulose acetates in chloroform,
(c) viscosity of the nitrocellulose in ether-alcohol solution.

Preparation of Standard Cellulose.

(a) *From Cotton.*—The methods of Schwalbe (*Chemie der Cellulose*, 1911, p. 602 and *Farb. Ztg.*, 1913, 436) Robinoff and the American Chemical Society—Cellulose Division (*Ind. Eng. Chem.*, 1923, **15**, 748) recommend the use of a bleaching agent for the preparation of standard cellulose from cotton, but as it is difficult to prevent the action of bleaching agent on the cellulose itself the use of such chemicals has been avoided in this work and the method of Correy and Grey (*Ind. Eng. Chem.*, 1924, **16**, 852) has in general, been followed.

The alcohol-benzol extracted cotton was treated with a large volume of caustic soda solution (1%) with careful exclusion of air. The ash content was diminished by treatment with acetic acid. When the same procedure was applied to jute cellulose delignified by the chlorine peroxide method, it was found that the impurities could not be efficiently removed and the cellulose matter had to be subjected to the action of 17·5% cold alkali. In order to make the conditions comparative for cotton cellulose, the cellulose as prepared above from cotton was also subjected to the action of 17·5% alkali under the same conditions as for jute cellulose.

(b) *From Jute.*—Delignification of jute was effected by the chlorine peroxide method as previous experience in this laboratory (Chowdhury and Majumder, *J. Indian Chem. Soc.*, 1929, **6**, 139) has shown that jute cellulose is little affected by this treatment. The delignified jute was then subjected to the action of 5% boiling alkali or 17·5% cold alkali. It was however found that neither method removed the hemicelluloses completely and that a part of the furfural-yielding complex remained in the residual cellulose, the minimum furfural value thus obtained being 2·5%. By a combination of the two processes, *i.e.* by alternate treatment for half an hour with cold concentrated alkali and boiling dilute alkali, the furfural value is reduced to 1·8%. Further reduction of the furfural value can be effected by continued previous extraction of the delignified fibre with boiling water, followed by alternate treatment with 17·5% cold alkali and 5% boiling alkali. By this treatment the furfural value is reduced to 0·25%

which compares very favourably with that of standard cotton cellulose as prepared by the above method. During the treatment with alkali, exposure to air was carefully avoided in order to prevent any consequent oxidation. The standard celluloses as obtained above were tested by means of its furfural value and their solubility in 17.5% cold alkali. The data in the following table represents the results obtained.

TABLE I.

Cotton cellulose.

Treatment.	Furfural.	Solubility in 17.5% cold alkali.
Raw cotton extracted with alcohol-benzol	1.8%	15.0%
Do treated once with 17.5% alkali	0.702	9.6
Do 5 times	0.31	2.5
Do and boiled twice with 5% alkali	0.29	1.9

TABLE II.

Jute cellulose: Treatments showing progressive reduction in furfural value and solubility in alkali.

Treatment.	Furfural.	Solubility in 17.5% alkali.
Delignified jute	9.6%	32.77%
Do treated once with 5% boiling alkali	3.4	22.58
Do treated 5 times	2.5	18.0
Do treated once with 17.5% cold alkali	2.5	18.45
Do treated 5 times	1.8	14.05
Delignified jute after 3 extractions with boiling water only	5.39	23.71
Do and then given one treatment with 17.5% cold alkali	1.02	10.08
Do and then given 4 successive similar treatments	0.31	1.65
Do further boiled twice with 5% alkali	0.25	1.83

TABLE III.

Analysis of the two purified celluloses.

			Jute.	Cotton.
Lignin	nil	nil
Furfural	0.25%	0.29%
Fats and resin	nil	nil
Ash	0.19%	0.1628%
Moisture	10.01%	8.3372%
Uronic acid	nil	nil
Solubility in 17.5% alkali			1.82%	1.9%

Acetylation.

It is well known that during acetylation the reagents and the temperature employed considerably affect the cellulose. We have therefore endeavoured to use a method of acetylation which would have the least possible action on cellulose itself. Only very few methods are available for such acetylation. As the methods represented in E.P. 297766 (1928) or that of Hess (*Ber.*, 1928, 61, 461) require high temperature or a prolonged period for complete acetylation, the authors adopted the method of Barnett as modified by Irvine and Hirst (*J. Chem. Soc.*, 1922, 121, 1585). It was however found that this method if carried out at high temperature, as recommended by these authors, causes disintegration and partial decomposition of the product obtained from jute cellulose. If however the proportion of the reagents be slightly increased, it is possible to carry out the reaction at a much lower temperature when no such disadvantages are experienced and no reducing matter is found in the filtrate after precipitation of the acetate in water.

10 G of air-dried, finely shredded jute cellulose were placed in a stoppered bottle and incorporated with 65 c.c. of glacial acetic acid through which a stream of dry chlorine was passed for 40-50 seconds. After standing for $\frac{1}{2}$ hour, acetic anhydride (70 c.c.) was added and sulphur dioxide gas bubbled through the mixture for $1\frac{1}{2}$ minutes and the bottle stirred mechanically. After 3 to 4 hours, the cellulose gelatinised and began to dissolve slowly. Finally to hasten the reaction, the temperature was raised to 40°. The solution, when quite clear, was treated with chloroform, and water in the manner recommended by Irvine and Hirst (*loc. cit.*). The whole procedure required some 35-40 hours. If however the

cellulose is previously dipped for about 1 hour in glacial acetic acid, pressed and dried in the air, the time of the reaction can be reduced to 20-24 hours. As this latter treatment might to some extent affect the cellulose, we have preferred not to use it during acetylation.

The acetyl content of the product was determined as follows : A weighed quantity of the acetate was boiled for 2 hours with a known excess of standard caustic soda solution, the excess of alkali being titrated with standard sulphuric acid. Owing to possible chemical action or the adsorption of caustic soda in the regenerated cellulose, each result was corrected by means of a control experiment in which pure cellulose was treated with caustic soda solution under the same conditions.

Some typical results are quoted :

(I) 0.4914 G. of jute acetate required 11.0032 c.c. of $N/2$ - caustic soda while 0.5804 c.c. was used for control experiment. The percentage of acetyl therefore was 45.6.

(II) 0.8188 G. of jute acetate required 17.529 c.c. of $N/2$ - caustic soda and the control experiment took 0.6214 c.c. The percentage of acetyl was 44.42.

(I) 0.4283 G. of cotton acetate took 9.9338 c.c. of $N/2$ - alkali while 1.0684 c.c. were used for control experiment. The percentage was therefore 44.5.

(II) 0.4150 G. of cotton acetate took 9.6396 c.c. of $N/2$ - alkali while the blank experiment required 1.0684 c.c. The percentage was therefore 44.4.

The detailed results obtained are given in the following table.

TABLE IV.

	Jute		Cotton	
Cellulose (g.)	5	5	5	5
Water and ash-free cellulose (g.)	4.49	4.49	4.575	4.575
Acetate yield (g.)	7.8921	7.9011	8.0823	8.1031
Percentage of the yield	175.8	176.0	176.6	177.2
Theoretical value	177.7	177.7	177.7	177.7
Acetyl value	44.42	45.6	44.4	44.5
Theoretical acetyl value	44.8	44.8	44.8	44.8

Yield of Glucose.

As calculated from the yield of methylglucoside.—For the preparation of methylglucoside we have generally followed the

directions of Irvine and Hirst (*loc. cit.*) with slight modifications, having used a temperature of 135-40° instead of 125° and also a higher acid content (1.2%) in methyl alcohol in place of 0.75% recommended by them. With these modifications the time is reduced to 48 hours and the yield of glucosides is practically quantitative.

One part of acetate (nearly 4 g.) was treated in a sealed tube for 48 hours at 135-40° with methyl alcohol (15 parts) containing 1.2% hydrochloric acid. At the end of this period only a slight trace of solid remained undissolved in case of both jute and cotton celluloses and the liquid had assumed a faint golden yellow colour. The contents of the tube were then filtered, carefully neutralised with silver carbonate and decolourised with animal charcoal. Precautions were taken to recover any matter adhering to the filter paper and to the charcoal residues. Finally it was concentrated under reduced pressure (10 mm.) and left overnight in a calcium chloride desiccator, when it set to a solid mass. The last trace of solvent was driven away by means of hot dry air.

Finally it was dried in vacuum over calcium chloride to constant weight. We have here eliminated the distillation of the solvent under reduced pressure recommended by the above authors and thus avoided a tiresome process and the mechanical loss involved in it. The crystals melted between 125-48° and gave 15.92% methoxyl in case of glucoside from jute and 15.925% in case of glucoside from cotton. No mineral matter was present and no furfural was liberated on treatment with 12% hydrochloric acid (boiling). Details of two typical experiments are recorded for each particular cellulose.

TABLE V.

	Jute		Cotton	
Wt. of acetate (dry and ash-free) (g.)	3.8	3.779	3.805	3.892
Acid methyl alcohol used (1.2% HCl.) (c.c.)	60	60	60	60
Time (135-40°) (hr.)	48	48	48	48
Wt. of solid remaining in the sealed tubes (g.)	nil	0.082	nil	0.05
Permanent sp. rotation $[\alpha]_D^{28}$	106°	106°	107°	106°
Yield of dry crystals	2.56	2.49	2.549	2.534
Yield (%)	99.492	99.458	98.925	97.37
Methoxyl (%)	15.92	—	15.925	—
Equiv. glucose (%)	99.98	99.952	99.413	97.858

It will be observed from the above data that the yield from both cases is quantitative and is thus an improvement on 95.5% obtained by Irvine and Hirst. In calculating the yield, the weight of insoluble matter left in the tube after the reaction was deducted from the weight of cellulose taken. The melting point of the mixed glucosides varied from 125—148° according to the proportion of β -glucoside present. The purity of the methylglucoside was established by hydrolysis of the glucosides with 4% hydrochloric acid and noting the specific rotation of the glucose formed.

2.2614 G. of methylglucoside from jute cellulose were boiled under reflux with 25 c.c. of 4% hydrochloric acid solution for $\frac{1}{2}$ hour and the contents of the flask were then carefully made up to 100 c.c. The specific rotation obtained was $[\alpha]_D^{29} = 52.25^\circ$ ($\alpha = 1.096$, $l = 1$ dm., $c = 2.0982$), the corresponding figure for pure glucose being 52.5° .

A similar procedure was adopted in case of methylglucoside from cotton and the specific rotation was found to be $[\alpha]_D^{28.5} = 52.2^\circ$, showing thereby that both the glucosides are made up entirely of glucose residues.

That the methylglucosides from both jute and cotton consist only of glucose was further established indirectly in the following manner:

On recrystallisation of the mixed glucosides from absolute alcohol characteristic crystals of m.p. 165° and $[\alpha]_D^{29} = 157.6^\circ$ (in aqueous solution) were obtained ($\alpha = 1.84$, $l = 1$ dm., $c = 1.17$), the corresponding figure for α -methylglucosides being 165 – 166° and 157.5° respectively. The mother liquor after separation of the crystals of α -methylglucosides evidently contained a larger proportion of β -form. On heating this mother liquor again with 1.2% acid methyl alcohol for 48 hours in sealed tubes, the equilibrium between α - and β -forms was re-established and the specific rotation was found to be $[\alpha]_D^{28} = 106^\circ$. Evidently no other sugars except glucose are present in the mixed glucosides. As the theoretical yield of methylglucosides has been obtained both from the jute and cotton celluloses, it follows that both the celluloses are made up entirely of glucose, and no other hexose or pentose constitute an essential part in the molecules of the celluloses.

Hydrolysis with sulphuric acid.—Attempts were then made to ascertain the maximum yield of glucose obtained by the hydrolysis of the two celluloses under identical conditions. For this purpose the well known method of Monier Williams was followed in preference to the method of Keisel and Semiganoski (*Trans. Chem.*

Pharm. Inst. Moscow, 1927, 18, 82) who claim 100% yield of glucose from cotton cellulose, as they did not isolate the sugar in crystalline form.

5 G. of the cellulose were dissolved in 30 c.c. of 72 % sulphuric acid and the dark coloured viscous solution was allowed to remain 1 week at room temperature. The sulphuric acid solution was diluted to 3 litres with water and boiled continuously under reflux for 15 hours. A small amount of dark coloured flocculent precipitate was found in the liquid. This was filtered off, dried and deducted from the weight of the cellulose used. After boiling, the almost colourless liquid was neutralised with barium hydroxide, filtered clear from the sulphate and evaporated to dryness by distilling at a low temperature under reduced pressure (10 mm.). A slight alkalinity developed during evaporation which was always made neutral by means of N/10-sulphuric acid. The residue from the distillation was extracted with pure methyl alcohol, filtered and decolorised with animal charcoal. The solution was then concentrated under reduced pressure but it was very difficult to crystallise the syrup even after passing hot dry air through the mass. Crystallisation however took place on the addition of a very small amount of pure glucose. From this crude product glucose was purified by recrystallisation from absolute alcohol and was tested by means of its melting point and that of its osazone. For the sake of comparison, the data are represented below :

TABLE VI.

	Jute		Cotton	
Wt. of cellulose (g.)	5	5	5	5
Wt. of ash-free dry cellulose (g.)	4.49	4.49	4.575	4.575
Wt. of glucose obtained (g.)	4.7055	4.6336	4.8952	4.8312
Yield (%)	104.8	103.2	107.0	105.6
Theoretical value (%)	111.1	111.1	111.1	111.1
M.p. of glucose	145°	146°	144°	145°
M.p. of the osazone	204°	205°	205°	205.5°

Yield of Cellobiose Octa-acetate.

The yield of cellobiose octa-acetate from both jute and cotton was next ascertained, as this question has an important significance in regard to the constitution of cellulose.

The highest yield of cellobiose octa-acetate found from cellulose material is 50% obtained by Hess and Frieze (*Annalen*, 1927, **456**, 38), but as this process is tedious and as other investigators have not been able to obtain the same high yield by following their directions, we preferred to follow the method of Spenser (*Cellulosechem.*, 1929, **10**, 61) who obtained a maximum yield of 46.5%. The best yield was obtained at 50° with 0.2 c.c. of sulphuric acid (*d* 1.84) after a period of 15 days, the maximum yield of cellobiose octa-acetate from jute being 41.14% while that from cotton was 43.8%.

8 C.c. of acetic anhydride were taken in a stoppered conical flask and cooled to 0° and 0.6 c.c., 0.4 c.c., 0.2 c.c. of sulphuric acid (*d* 1.84) was cautiously added in three different cases without causing any appreciable rise of temperature. 2 G. of jute and cotton celluloses were separately added to the reagent mixture, which was then cooled for 30 minutes and kept at room temperature until the maximum yield was obtained. The product was recrystallised from alcohol and showed the characteristic reactions of cellobiose octa-acetate. Under the microscope, a drop of the hot solution gave characteristic rosettes of needles. Both the samples melted at 226° and 227° and gave the specific rotation $[\alpha]_D^{29} = 41.5^\circ$ and 41.6° respectively in chloroform solution.

TABLE VII.

Yield of cellobiose octa-acetate.

Cellulose used.	Temp.	Sulphuric acid (<i>d</i> 1.84).	Days.	Maximum yield.
Jute	39.5-40°	0.2 c. c.	25	15.4%
Cotton	"	"	25	22.2
Jute	"	0.4	25	35.1
Cotton	"	"	25	35.1
Jute	"	0.6	15	29.3
Cotton	"	"	15	28.3
Jute	50°	0.2	15	41.14
Cotton	"	"	"	43.8

Although the mechanism of acetolysis of celluloses is not clearly understood and the period of reaction is comparatively long, the agreement in the maximum yield of cellobiose octa-acetate is quite satisfactory and points to the identity of two celluloses from the chemical point of view.

Methylation of Cellulose.

Attention was then directed to the maximum methoxyl content in the methylcellulose from jute. In the preliminary experiments, the tedious method of Denham and Woodhouse (*J. Chem. Soc.*, 1921, 119, 77) with the modification of Irvine and Hirst (*J. Chem. Soc.*, 1923, 123, 528) for the methylation of cellulose was followed, but the maximum yield of methoxyl obtained in case of jute after thirteen repeated alkylations was only 32.5% and this value could not be appreciably increased even after seventeen methylations. As this value is considerably lower than the theoretical maximum (45.5 %), we followed Urban's method (*Cellulosechem.*, 1926, 7, 73) for the methylation of lignin from spruce wood. The method applied to jute cellulose gave very satisfactory results and a methoxyl content of 44.3% was obtained after 10 operations, a value which could not be substantially increased after repeating the process 15 times (theoretical, 45.5 %). It may be noted here that the maximum methoxyl value obtained by Irvine and Hirst (*loc. cit.*) in the case of cotton cellulose was 43.1 to 44.5%.

5 G. of finely shredded jute cellulose were dipped in 150 c. c. of 45 % caustic potash solution in a stoppered bottle and shaken vigorously in a shaking machine for 6 hours. It was then cooled with ice and salt and dimethyl sulphate (5 c. c. at a time) was added at intervals of $\frac{1}{2}$ hour. The procedure was continued with occasional shaking until the mixture was acidic. It was then washed well first with distilled water and then with alcohol and ether and dried in vacuum over sulphuric acid.

This method has the advantage over that of Irvine and Hirst (*loc. cit.*) that in this case no ethereal solution of dimethyl sulphate is required. The process is conducted at a lower temperature with less dimethyl sulphate and with less fear of disintegration of the product. The use of alcoholic alkali accompanied by a sudden rise of temperature is avoided.

Differentiation of the two Celluloses by means of the Viscose Reaction.

Lieser (*Cellulosechem.*, 1929, 10, 21) has been able to characterise different celluloses by means of the above reaction. He has shown that the cellulose-A, which is soluble in alkali, requires a minimum concentration of only 7.5 % caustic soda to form alkali cellulose and undergo subsequent reaction with carbon disulphide to form viscose, while cotton cellulose requires a minimum concentration

of 16 % caustic soda for the above purpose, intermediate concentrations being necessary for other types of celluloses.

In the following experiments the concentration of alkali was varied from 10% to 17.5% in order to ascertain the minimum strength necessary for mercerisation of each of the two celluloses which would then react with carbon disulphide to form viscose.

It was found that a different strength of alkali was necessary in each case and that for the same strength of alkali, the residue obtained after the formation of viscose was always greater in the case of cotton than that in the case of jute. This may be attributed to the greater resisting power of cotton, due mainly to physical difference in composition and arrangements of the micels. The solubility, viscosity, the time required for coagulation of viscose solutions prepared from the two celluloses were, however, widely different.

For the preparation of viscose we have used the following two methods:

(A) 1 G. of the cellulose was dipped in 20 c. c. of alkali for 3 days, the excess of the alkali pressed out, carbon disulphide added and the mixture agitated in a shaking machine for a few hours. The reaction product was then dissolved in 5 % alkali, 10 c. c. being added every $\frac{1}{2}$ hour. The solution was made upto 100 c.c. and filtered in a tared gooch crucible through fine muslin.

(B) 1 G. of cellulose was dipped first in carbon disulphide for 1 hour, the excess poured off and 20 c.c. of alkali of desired strength were added and shaken for 1 hour. It was then made upto 100 c.c. with 5% solution of caustic soda in the usual manner. The results obtained are given in the following table.

TABLE VIII.

Properties of viscose prepared by the methods (A) and (B).

Fibre.	Alkali conc.	Residue (g.).		Viscosity sec. (Ostwald).		Coagulation days.	
		A	B	A	B	A	B
Jute	15% NaOH	nil	nil	20'43"	28'25"	5	7
Cotton	"	0.1812	0.052	35'7"	58' 2"	2	3
Jute	12% "	0.208	nil	3'12"	4'39"	27 hr.	39hr.
Cotton	"	0.602	0.442	5'24"	12'38"	24 hr.	24hr.
Jute	10% "	0.639	0.212	43"	68"	36 "	24 "
Cotton	"	0.87	0.85	75"	98"	24 "	24 "

*Surface Tension of the Viscoses prepared from Jute and
Cotton Celluloses.*

As it was suspected that the variation in physical properties e.g., viscosity, solubility, coagulation, etc., of the above viscose solutions might be due to the character and size of the micellae composing the two celluloses, it was thought advisable to test the surface tension of the two solutions. It is known that the surface tension diminishes with the thickness of films formed at the surface of a solution at different intervals. As the formation of such films is due to collection of micellae, it was thought likely that the surface tension would diminish as the micellae accumulate at the surface. The method used for determination of the surface tension is that developed by Ghosh and Dutt (*J. Indian Chem. Soc.*, 1929, 6, 103) in this laboratory who observed similar changes in surface tension of solutions of different dyestuffs and attributed to the formation of micellae.

The experimental details are the same as those of the above authors. The viscose used for this purpose was prepared from the two celluloses by the method (B) previously described using 17.5% alkali, the solution obtained from 1g. of cellulose being made upto 500 c.c. with distilled water. The variation of the surface tension with time was then noted, surface tension being calculated as follows:—

$$\text{Surface tension of the solution} = \frac{\sigma W_2}{W_1}$$

where σ is the surface tension of water at the temperature of the experiment, W_2 is the weight required to raise the basin from the surface of the solution, and W_1 is the weight required to raise the basin from the surface of water.

As coagulation took place after some time (which may be attributed to increase in the size and number of micellae), we could not observe the minimum surface tension. Our object was however attained by the character of the curve obtained in the two cases. The results obtained are noted in Table IX and are further brought out in the plotted curve on the next page.

FIG. 1.

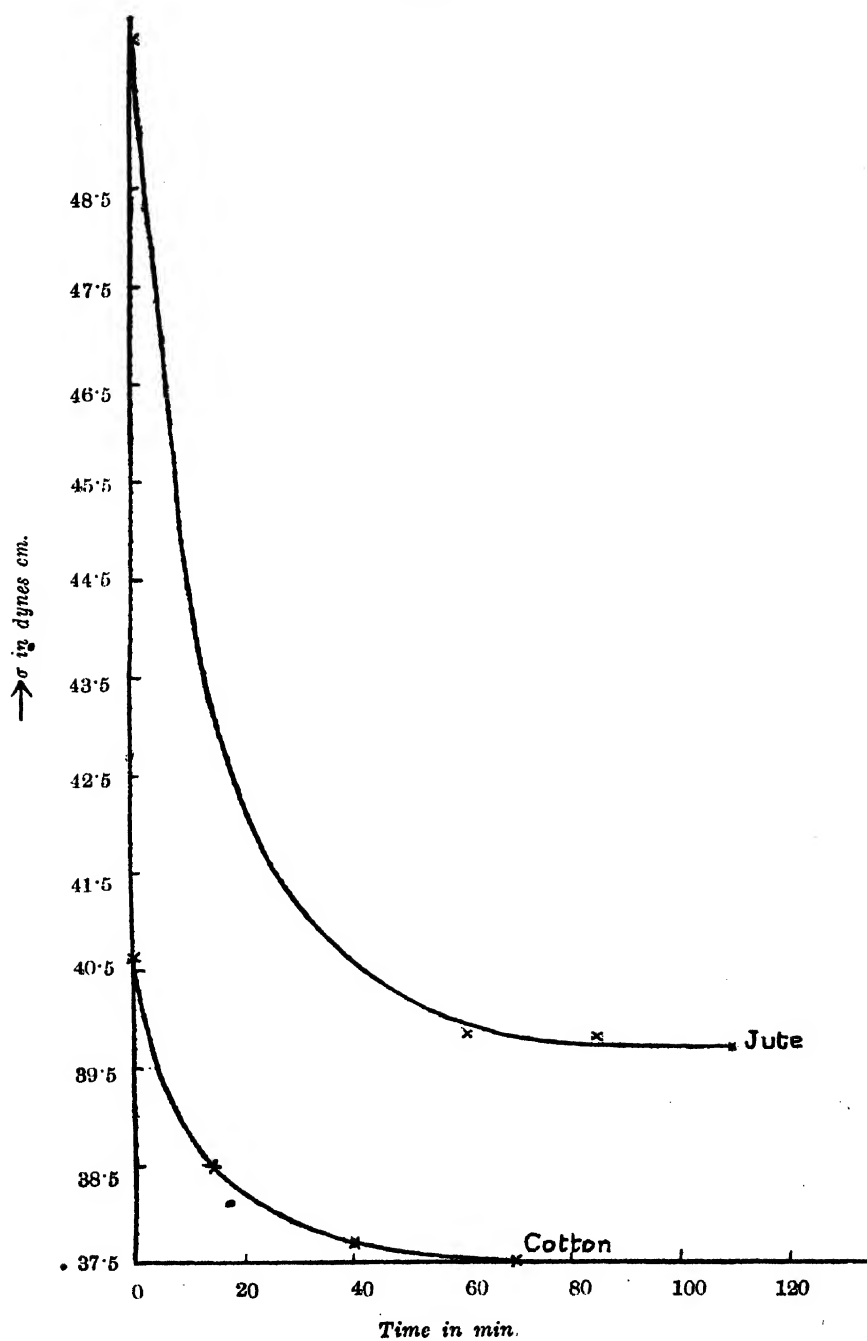


TABLE IX.

*Surface tension of viscose solutions made from jute.*Temp. = 29.2°. $\sigma = 71.18$. $W_1 = 2.108$.

Time (min.)	...	0	20	42	61	85	110
W_2	...	1.48	1.3	1.2	1.18	1.179	1.178
Surface tension of viscose	...	49.98	42.89	40.52	39.85	39.81	39.71

TABLE X.

*Surface tension of viscose solutions made from cotton.*Temp. = 29.2°. $\sigma = 71.18$. $W_1 = 2.108$.

Time (min.)	...	0	14	40	70
W_2	...	1.208	1.125	1.117	1.111
Surface tension of viscose	...	40.62	38.48	37.70	37.52

Particular attention may be drawn to the higher surface tension of jute viscose. This phenomenon may be attributed to the smaller size of micellae or to a smaller molecular weight of the molecules composing jute fibre owing to the smaller degree of polymerisation of glucose units. The two curves are, however, similar in character which indicates similar changes taking place in the viscose solutions on standing and suggests a similarity in chemical constitution.

It may be noted that viscose made from cotton cellulose coagulates in a shorter time than jute viscose in which the particles or micellae in colloidal solution are evidently smaller in size.

Viscosity Tests.

Cupra-ammonium solution.—(a) The cupra-ammonium solution was made according to the directions of Hibbert and Parson (*J. Soc. Chem. Ind.*, 1925, **44**, 483r). Cupric hydroxide was first prepared by cautiously adding slight excess of ammonium hydroxide to a concentrated filtered solution of boiling copper sulphate solution. The precipitate was allowed to settle, washed by decantation with hot water, cooled below 10° by the addition of a few lumps of ice, and

then sufficient 9% caustic soda was slowly introduced with stirring until the deep blue colour of copper hydroxide was formed. The precipitate was then filtered, washed free from alkali with cold water and then with alcohol and water. It was dried in the air for several days and passed through a 40-mesh sieve.

4 G. of an air-dried sample of cellulose were introduced into a stoppered bottle along with 4 g. of copper hydroxide as prepared above, 225 c.c. of a 28% ammonium hydroxide solution were then added, the bottle stoppered and the mixture shaken mechanically. Viscosity was measured by means of the Ostwald apparatus. It was found that the viscosity of the solution obtained from jute was lower (8' 28" at 29°) than that from cotton (10' 24" at the same temperature).

(b) The same result was obtained by observing the viscosity of cellulose acetate in chloroform. A 6.4% cellulose acetate solution in chloroform was found to have a viscosity of 3' 35" at 29.5° in the case of jute and 28' 52" at the same temperature in the case of cotton.

(c) 1% Solution of nitrocellulose in ether-alcohol (55:45) gave a viscosity (at 20°) of 4" in the case of cotton and 0.5" in the case of jute, when determined by the falling sphere viscometer of Gibson and Jacobs.

Solubility tests.—While preparing the cupra-ammonium solution as described above, it was found that cotton cellulose required 1½ hours for complete solution while jute cellulose dissolved in ½ hour. In the case of cellulose acetate it was found that the product obtained from cotton was not easily soluble in chloroform, a 6.4% solution being obtained with some difficulty while the acetate obtained from jute cellulose under identical conditions was easily soluble. The same remarks are applicable to nitrocelluloses prepared from jute and cotton, the former being easily soluble in alcohol-ether and in acetone while nitrocellulose prepared under identical conditions from cotton was soluble with difficulty.

It may be noted here that the lower viscosity and higher solubility of different derivatives obtained from jute cellulose are interesting also from certain industrial points of view, as several industries, particularly the lacquer industry, prefer cellulose derivatives of low viscosity and high solubility in order that coating compositions may be prepared with maximum content of cellulose acetate or cellulose nitrate.

Summary and Conclusions.

It will be evident from the experiments described above that chemical tests indicate the identity of jute and cotton celluloses. Thus, practically the same yield of cellulose acetate is obtained in both cases, the yield of glucose as determined by the yield of methyl-glucoside is practically quantitative and the yield of crystalline glucose is almost identical in both instances. The same observation is true of the yield of cellulose octa-acetate and the percentage of methoxyl in methylated cellulose. It may, however, be observed that there is a slight difference in the behaviour of the two celluloses when tested by means of alkali of different concentrations with the subsequent formation of viscose. The difference is, however, more prominent in the case of physical tests *e.g.*, surface tension, viscosity, solubility and the time of coagulation of viscose solutions. These differences are not without significance on the constitution of cellulose.

Cellulose is usually represented by the formula $(C_6H_{10}O_5)_n$, 'n' being unknown. The usual assumption that 'n' is a very great number is contradicted by recent works of Pringsheim (*Annalen*, 1926, **448**, 163), Karrer (*Cellulosechem.*, 1921, **2**, 127), Hess and co-workers (*Annalen*, 1926, **448**, 104), Irvine and co-workers (*J. Chem. Soc.*, 1923, **123**, 518) as well as by the röntgenographic investigations of Herzog and others, which point to the probability of 'n' being a very small figure lying between 1 and 4. On the other hand the investigations of Staudinger and his co-workers (*Z. Phys. Chem.*, 1927, **126**, 425) as well as of Meyer and Mark (*Ber.*, 1929, **62**, 1103) make it highly probable that cellulose is formed by the polymerisation of the glucose unit and that the degree of polymerisation is probably very high and may differ in different cases.

According to these latter investigators some 30-35 glucose molecules are linked with one another by means of the main valency along the axis of the fibre in the form of a chain while some 40-60 chains are linked side by side by means of the secondary valency of hydroxyl groups to form a micell, several of these micellae forming the cell of the fibre.

The results obtained in the foregoing experiments give support to the latter view. It appears highly probable that the degree of polymerisation (or at least the size of the micellae) is different in different cases. The degree of polymerisation in the case of jute

cellulose is evidently lower than in the case of cotton. This would explain the higher surface tension, lower viscosity and greater solubility in the case of jute cellulose derivatives.

Though it is evident from the above investigations that purified cellulose from jute and that from cotton give identical results from the chemical point of view, it would be premature to say at this stage that they are identical in all respects. Both jute and cotton celluloses consist of poly-anhydroglucose residues, each glucose unit being probably linked to another in exactly the same manner. But the number of glucose residues constituting a poly-anhydroglucose unit appears to be different in the two cases.

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On Thioaldehydes and Thioketones. Part I.

By SUSIL KUMAR MITRA.

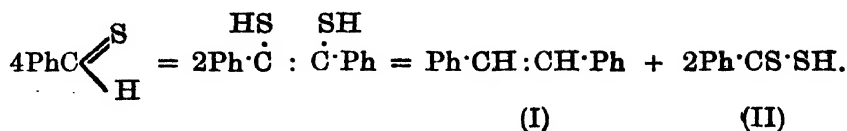
The simple replacement of the oxygen atom in an aldehyde, *e.g.*, benzaldehyde by sulphur has always resulted in the production of a polymerised body (*cf.* Baumann and Fromm, *Annalen*, 1848, **66**, 158 *et seq*; Klinger and others, *Ber.*, 1877, **10**, 1877 *et seq*). Barbaglia and Marquardt's attempt (*Ber.*, 1891, **24**, 1881) resulted in a similar failure, benzaldehyde when heated with sulphur gave stilbene and trithiobenzaldehyde.

Benzylidene chloride when condensed with sodium sulphide in the present investigation, furnished a reddish oil which decomposed when distilled *in vacuo* to stilbene.

Ethyl thioacetoacetate and benzaldehyde when condensed in presence of piperidine furnished an oil which solidified (m.p. 82-83°) after 24 hours. The analysis corresponded to a thiobenzaldehyde, probably polymerised. From the mother liquor diethyl benzal-diacetoacetate can be isolated. Hence it seems that ethyl thioacetoacetate parted with the sulphur atom abstracting the oxygen atom from benzaldehyde. The liberated ethyl acetoacetate reacted with benzaldehyde in the normal Knoevenagel way. This is in conformity with the behaviour of this substance, as the sulphur atom is loosely bound. Benzaldehyde does not react with ethyl thioacetoacetate without the condensing agent even on boiling.

The substance (m.p. 82-83°) condenses with phenylhydrazine, methylphenylhydrazine and hydrazine hydrate to give the corresponding benzylidene derivatives which point to the substance not being a thioether. Klinger (*loc. cit.*) and Ruheman (*J. Chem. Soc.*, 1905, **87**, 25) isolated a substance having the same m.p. (83-84°), which was regarded as a mixture of various indefinitely polymerised products (*Ber.*, 1891, **24**, 1431). The ready reaction of the compound with phenylhydrazine suggests that the molecules are loosely bound in the polymerised product by residual affinity. The substance (m.p. 82-83°) is converted to β -trithiobenzaldehyde of Baumann and Fromm by acid chloride even at 0°.

The substance when boiled in chloroform solution with piperidine produced stilbene and hydrogen sulphide.



The substance (II) could not be isolated and probably is responsible for the liberation of hydrogen sulphide.

Anisaldehyde under identical conditions furnished thioanisaldehyde (m.p. 73-75°); identical with that obtained by passing sulphuretted hydrogen over anisaldehyde. By performing similar experiment (benzaldehyde and ethyl thioacetoacetate) in alcoholic solution saturated with hydrochloric acid, Fromm's β -trithiobenzaldehyde was isolated quantitatively. *o*- and *m*-Nitrobenzaldehydes with alcoholic hydrochloric acid gave corresponding thioaldehydes in the amorphous state. Thioacetophenone was isolated as a dark violet oil (b. p. 110°/20 mm.) by passing hydrochloric acid gas through alcoholic solution of ethyl thioacetoacetate and acetophenone. Benzophenone on similar treatment yielded thiobenzophenone as a blue oil (b. p. 155°/10 mm.). Thiobenzaldehyde and thioanisaldehyde were found to have molecular weights corresponding to $(\text{C}_6\text{H}_5\text{CHS})_7$ and $(\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHS})_{11}$ respectively, but thiobenzophenone was found to be monomolecular. This suggests that these thioaldehydes were produced in the unimolecular state and were polymerised subsequently. It was observed that these aldehydes gave readily hydrazones when treated with excess of hydrazines alone or in pyridine solution containing a trace of piperidine. Evidently these bases possess the property of transforming the polymerised molecule to the unpolymerised state.

EXPERIMENTAL.

Thiobenzaldehyde (Method I).—Thioacetoacetic ester (10 g.) in alcohol (50 c. c.) was mixed with benzaldehyde (20 g.). The solution was diluted with water to turbidity. Piperidine (0.5 c.c.) was then added and the mixture was allowed to stand overnight. The supernatant liquid was then decanted off and the white precipitate which remained at the bottom was washed several times with dilute alcohol and dissolved in chloroform and finally precipitated by means of petroleum ether, m.p. 83-84° (*cf.* Baumann and Fromm, *Ber.*, 1891, 24,

1481), yield 70 p.c. It is soluble in chloroform, carbon disulphide and piperidine. It dissolves on boiling with alcoholic sodium ethoxide to a deep red solution. A boiling aqueous alcoholic solution of potassium cyanide does not affect it (8 hours). On shaking with metallic mercury or freshly prepared mercuric oxide it gave mercuric sulphide. (Found: C, 68.1; H, 5.2; S, 25.5; M. W. (ebulliscopic in chloroform), 814.5. $(C_7H_6S)_7$ requires C, 68.8; H, 4.9; S, 26.2 per cent; M. W., 854).

Ethyl benzaldiacetoacetate.—The decanted supernatant liquid from above was treated with water to just turbidity and on keeping overnight, crystals of ethyl benzaldiacetoacetate began to appear. Recrystallised from alcohol and petroleum ether, it melts at 138°. (Found: C, 65.2; H, 7.1. $C_{19}H_{24}O_6$ requires C, 65.5; H, 6.9 per cent.).

Benzaldehyde-phenylhydrazone.—Thiobenzaldehyde (5 g., 1 mol.) and phenylhydrazine (1 mol.) were heated in a boiling water-bath for 6 hours. When the evolution of hydrogen sulphide ceased, the product was washed with dilute hydrochloric acid and crystallised from alcohol, m. p. 158°, yield 80 p. c. (Found: N, 14.57. $C_{13}H_{12}N_2$ requires N, 14.3 per cent.).

Benzaldehyde-asym-phenylmethylhydrazone.—Thiobenzaldehyde (5 g.) was treated with requisite quantity of phenylmethylhydrazine (asym.). The product was recrystallised from alcohol, m.p. 102°, yield almost theoretical. (Found: N, 13.51. $C_{14}H_{14}N_2$ requires N, 13.33 per cent.). It also gave *dibenzalazine* with hydrazine hydrate, m. p. 93°.

Thiobenzaldehyde (Method II).—Benzaldehyde (50 g.) in alcohol (10 c.c.) was treated with piperidine (1 c.c.) and hydrogen sulphide was passed into the mixture. After a short time, the mixture grew hot and the reaction was moderated by cooling in ice. The reaction was completed in 1 hour when most of the thiobenzaldehyde separated as a pasty mass. The product was then kept in a steam oven for 6 hours and finally crystallised from chloroform and alcohol, m. p. 83-84°, yield 90 p.c. Thioanisaldehyde was prepared in a similar manner, m.p. 78-75°.

Action of thiobenzaldehyde on acyl chlorides in presence of piperidine.—A mixture of thiobenzaldehyde (3 g.), piperidine (0.5 c.c.) and chloroform (30 c. c.) was allowed to stand for 6 hours and then treated with benzoyl chloride (1 mol.) and kept at 4° for 4 hours. It gave white crystals, m. p. 226°, identified as β -trithiobenzaldehyde, yield quantitative. Acetyl chloride behaves similarly.

Formation of stilbene from thiobenzaldehyde.—Thiobenzaldehyde (10 g.) dissolved in minimum quantity of chloroform and treated with piperidine (0.5 c. c.) and boiled on the steam bath till the evolution of hydrogen sulphide ceased. The chloroform was removed and the resulting product was extracted with ether; after removal of ether, the oil gave stilbene, m. p. 127° , on vacuum distillation.

Preparation of β -trithiobenzaldehyde.—Ethyl thioacetoacetate (13 g.) and benzaldehyde (10 g.) in alcohol (40 c.c.) were treated with dry hydrochloric acid gas till saturation. The whole mass was kept overnight. Needle-shaped crystals of β -trithiobenzaldehyde collected at the bottom. The product was recrystallised from acetic acid, m. p. 226° , yield 6 g. The m. p. remained unchanged on mixing with β -trithiobenzaldehyde prepared by passing sulphuretted hydrogen through benzaldehyde in alcoholic hydrogen chloride. It did not give any sulphuretted hydrogen when boiled with phenylhydrazine in acetic acid, in pyridine and in pyridine with a trace of piperidine.

o-Nitrothiobenzaldehyde.—*o*-Nitrobenzaldehyde (10 g.) in alcohol (50 c. c.) containing ethyl thioacetoacetate (11 g.) was treated at 0° with dry hydrogen chloride till saturation. After 8 hours a white precipitate separated. It was filtered off, washed free from acid with rectified spirit and then with alcohol and ether. It was purified by dissolving in pyridine and precipitating by means of ether, m. p. $168-72^{\circ}$, yield 9 g. (Found: N, 8.2; S, 19.2. $C_7H_5O_2NS$ requires N, 8.38; S, 19.16 per cent.).

o-Nitrothiobenzaldehyde is insoluble in almost all organic solvents excepting pyridine. On standing it transformed into plastic state and finally resinified. In pyridine solution in presence of few drops of piperidine it gave with phenylhydrazine the phenylhydrozone, m. p. 156° with evolution of sulphuretted hydrogen. (Found: N, 17.3. $C_{13}H_{11}O_2N_3$ requires N, 17.4 per cent.).

m-Nitrothiobenzaldehyde was prepared from *m*-nitrobenzaldehyde (5 g.) under similar conditions as the preceding compound. Its method of purification and properties are also similar to the *ortho* analogue. It shrinks at 110° and melts at $185-90^{\circ}$. (Found: N, 8.4; S, 18.9. $C_7H_5O_2NS$ requires N, 8.38; S, 19.16 per cent.).

Thioanisaldehyde.—An alcoholic solution (40 c. c.) of anisaldehyde (10 g.) and ethyl thioacetoacetate (20 g.) was saturated at 0° with HCl for 20 minutes and kept for 4 hours. After addition of water (4 c.c.) the pasty mass was washed with alcohol and extracted

with ether and ether removed. It was further purified by precipitating from hot alcohol, m. p. $73-76^{\circ}$, yield 4 g.

It can also be prepared with better yield (8 g.) by following the first method of preparation of thiobenzaldehyde. It is fairly soluble in ether, chloroform, pyridine and benzene, but sparingly soluble in cold alcohol. It gives phenylhydrazone, m. p. 120° . (Found: C, 65.3; H, 5.4; S, 20.8; M. W. (ebulliscope in CHCl_3), 1690. $(\text{C}_8\text{H}_8\text{OS})_{11}$ requires C, 68.15; H, 5.26; S, 21.05 per cent; M. W., 1672).

Thioacetophenone.— A mixture of acetophenone (50 g.) and ethyl thioacetoacetate (70 g.) in alcohol (100 c.c.) was saturated at 0° with HCl , allowed to stand for 10 hours and then treated with crushed ice. The oily product was extracted with ether, washed with sodium carbonate solution and dehydrated over calcium chloride. The oil on removing the ether was distilled in vacuum. The distillate between $100-125^{\circ}$ on repeated fractionation gave a dark violet oil, b. p. $110/20$ mm., yield 5 g. It is a deep violet unstable liquid possessing garlic odour. On keeping the colour disappears. Unlike the thioaldehydes it reacts with phenylhydrazine in cold with the formation of a phenylhydrazone, m. p. 102° . (Found: C, 70.2; H, 6.05; S, 23.3. $\text{C}_8\text{H}_8\text{S}$ requires C, 70.58; H, 5.88; S, 23.5 per cent.).

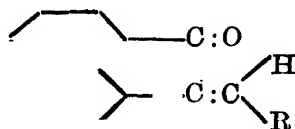
Thiobenzophenone was prepared from benzophenone (10 g.) and ethyl thioacetoacetate (15 g.) and purified in the same way as the preceding compound. The resulting oil was distilled in vacuum and the fraction collected between $100-170^{\circ}$ at 10 mm. on repeated fractionation gave a dark blue oil, b. p. $175/10$ mm., yield 3 g. (Found: C, 78.5; H, 5.1; S, 16.2; M. W., 213. $\text{C}_{13}\text{H}_{10}\text{S}$ requires C, 78.7; H, 5.05; S, 16.16 per cent; M. W., 198).

In conclusion the author wishes to convey his grateful thanks to Sir P. C. Rây for his kind interest and encouragement during this investigation.

Studies in Acenaphthenone. Part III. On the Reactivity of its 'CH₂' Group.

BY ANUKUL CHANDRA SIRCAR AND M.D. RAJA GOPALAN.

Recently some patents have been taken for the production of vat dyes by the condensation of acenaphthenone with 2:3-diketodihydrothionaphthene (D.R.P. 226244) and its derivatives (D.R.P. 218992) and with derivatives of isatin or naphthisatin (D.R.P. 237819; E.P. 27773/09). Kalle and Co. (E.P. 233452) have claimed the production of certain vat dyes by alkali fusion of acenaphthenone derivatives of general formula,



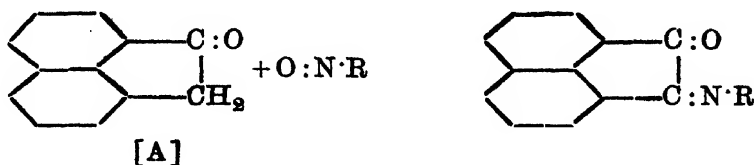
where R is a substituted or unsubstituted aryl group.

With the exception of these recent attempts to prepare vat dyes, very little or rather no systematic work has been done upon acenaphthenone derivatives. In the two previous communications in this series (*J. Indian Chem. Soc.*, 1932, 9, 103, 297) pyrilium, indole and acridine derivatives from acenaphthenone have been described. In the preparation of all the above three types of compounds both the CO and the CH₂ groups of acenaphthenone were utilised. The present paper deals with the reactivity of acenaphthenone through its CH₂ group alone.

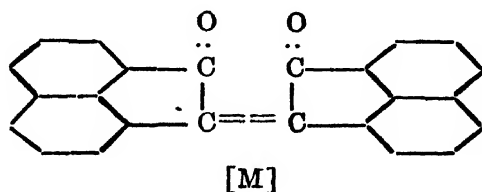
Action of Nitroso Compounds on Acenaphthenone.

Aromatic nitroso compounds very readily react with reactive methylene groups (cf. Ehrlich and Sachs, *Ber.*, 1899, 32, 2341; Sachs, *Ber.*, 1900, 33, 959; Sachs and Bry, *Ber.*, 1901 34, 118, etc.). Recently Pendse and Dutt (*J. Indian Chem. Soc.*, 1930, 8, 953) have shown that aromatic nitroso and isonitroso compounds in presence of glacial acetic acid or acetic anhydride condense with thiohydantoin forming products many of which are fairly

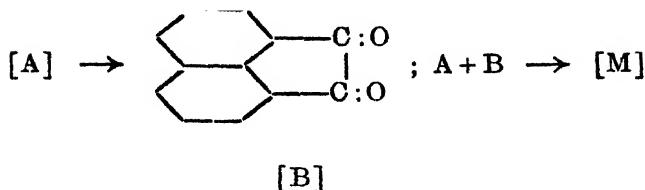
deep coloured and well adopted for dying on wool and silk. It was therefore expected that similar dyes could also be prepared by the condensation of acenaphthenone with various aromatic nitroso compounds.



In attempting to effect the condensation in presence of acetic anhydride, there was obtained every time only a dark resinous product from which nothing definite could be isolated. Glacial acetic acid and fused sodium acetate, 10% alcoholic potash, diethylamine, and piperidine were next tried as condensing agents and the following nitroso compounds were used: nitrosophenol, nitrosodimethylaniline and nitrosothymol. When the condensations were attempted at temperatures ranging between 60-80° using acetic acid and sodium acetate one and the same product, bisacenaphthylidenediketone (M), was obtained with every nitroso compound.



This compound had already been obtained by Graebe and Gfeller (*Annalen*, 1898, 276, 17) and afterwards been synthesised by the condensation of acenaphthenone with acenaphthenequinone (D.R.P. 212858). It has also been prepared in the course of the present investigation by condensing acenaphthenone with acenaphthenequinone and its identity established by mixed melting point determination and study of other properties. The formation of such a compound (*viz.*, bisacenaphthylidenediketone) can be explained only if a part of acenaphthenone is oxidised by the nitroso compounds to acenaphthenequinone which in turn condenses with the unchanged acenaphthenone.

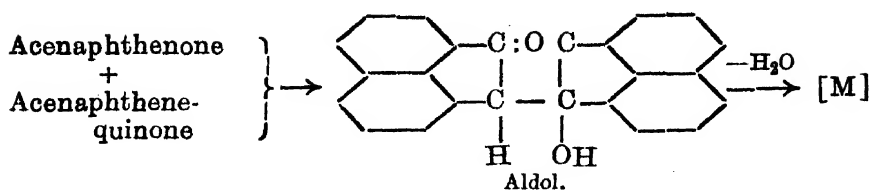


The oxidising actions of aromatic nitroso compounds have been already observed by many previous workers, *e.g.*, Alessandri (*Atti. R. Accad. Lincei*, 1915, v, 241, 62) found that asarone was oxidised to asarylaldehyde and apiol to apiolaldehyde by the action of nitrosobenzene. Again Cazeneuve (*Compt. rend.*, 1889, 109 185) showed that nitrosocamphor could oxidise glycerol to glyceric aldehyde, mannitol to mannitose and even alcohol to aldehyde.

When the reaction of the nitroso compounds with acenaphthene was attempted at ordinary temperature using acetic acid and sodium acetate, no change was observed even after keeping it for 3-4 days. When on the other hand the condensation was tried at ordinary temperature in alcoholic solution using 10% alcoholic potash, piperidine or diethylamine as condensing agents in addition to small quantities of the above mentioned compound (bisacenaphthylidenediketone), small quantity of another compound (white prismatic plates, m.p. 289-90°) was obtained. It contains no nitrogen. Its percentage composition agrees exactly with that of *acenaphthene*. Though the exact nature of the compound could not be established, it appears that two or more molecules of acenaphthene have somehow condensed without the elimination of any water. Further work towards the elucidation of the constitution of the substance will soon be undertaken.

Condensation of o-Diketones with Acenaphthene.

Reactive methylene groups can readily condense with carbonyl group (CO) to yield either an aldol type of product or the normal unsaturated product. Though a compound of the latter type has been prepared by the condensation of acenaphthene with acenaphthenequinone (D.R.P. 212858), the aldol type of compound had not been previously obtained and this has now been achieved. The aldol product on heating with sodium acetate and acetic anhydride loses a molecule of water and gives the normal unsaturated product.



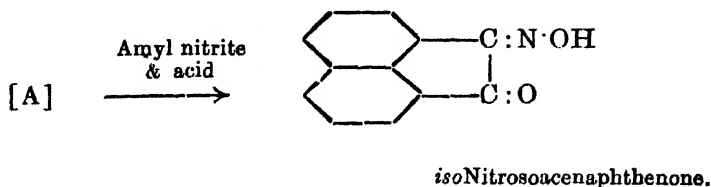
Acenaphthenone has also been condensed with phenanthraquinone but here only the aldol phase could be isolated. When condensation was tried with benzil the normal product was only obtained, the aldol phase being lost sight of.

Condensation of Aromatic Aldehydes with Acenaphthenone.

Graebe and Jequer (*Annalen*, 1896, **290**, 204) prepared benzyldeneacenaphthenone by the condensation of acenaphthenone with benzaldehyde. The work of Graebe and Jequer (*loc. cit.*) has now been extended and the following aldehydes were condensed with acenaphthenone:

(1) Anisic aldehyde, (2) salicylic aldehyde,* (3) *m*-hydroxybenzaldehyde, (4) *p*-nitrobenzaldehyde, (5) *m*-nitrobenzaldehyde, (6) *p*-acetylaminobenzaldehyde, (7) cinnamic aldehyde.

Action of amyl nitrite on acenaphthenone.—The reactivity of the CH_2 group towards amyl nitrite and hydrochloric acid has also been studied. By following the method adopted for the preparation of isonitrosoflavanone from flavanone (Kostanecki and Szabranski (*Ber.*, 1904, **37**, 2819), isonitroso derivative of acenaphthenone has been prepared. This is, as expected by theory, found to be identical with the monoxime of acenaphthenequinone.



* Kalle & Co. (E. P. 233452) claims the preparation of vat dyes by the potash fusion of certain acenaphthenone-aldehyde condensation products. But even in the original patent literature with the exception of the name of salicylic aldehyde derivative no mention is made about the compounds prepared or utilised.

EXPERIMENTAL.

Action of Nitroso Compounds on Acenaphthenone.

(a) *With p-nitrosodimethylaniline.*—To a mixture of acenaphthenone (0.5 g.) and freshly prepared *p*-nitrosodimethylaniline (0.43 g.) dissolved in 10 c.c. of acetic acid, 2.3 g. of fused sodium acetate were added. The mixture was heated on the water-bath for about 1½-2 hours when some orange needles began to separate. The heating was continued for another ½ hour to complete the separation of the crystals. These were filtered hot and recrystallised in beautiful orange needles from a large quantity of acetic acid in which they are only sparingly soluble, m. p. 287-88°. It does not contain nitrogen and was identified to be bisacenaphthylidenediketone (*vide infra*).

(b) *With nitrosophenol.*—Acenaphthenone (0.5 g.) and freshly prepared nitrosophenol (0.38 g.) were dissolved in 10 c.c. of acetic acid and 2.3 g. of fused sodium acetate added and the mixture refluxed on the water-bath for 3-4 hours. As in the preceding experiment, orange-yellow needles separated which after recrystallisation were identified to be bisacenaphthylidenediketone (*vide infra*).

(c) *With nitrosothymol.*—Acenaphthenone (0.5 g.) and nitrosothymol (0.52 g.) were dissolved in acetic acid to which 2.3 g. of sodium acetate had been previously added and proceeded as in the two preceding cases. The separated crystals were again found to be identical with bisacenaphthylidenediketone.

As the nitroso compounds acted as oxidising agents in the hot state, attempts were next made to bring about the desired condensation in the cold, but no change was observed even on standing for 3-4 days.

Then the condensation was tried in presence of condensing agents like alcoholic caustic potash, piperidine or diethylamine.

(d) *Action of nitrosophenol on acenaphthenone in presence of caustic potash.*—Acenaphthenone (0.5 g.) and nitrosophenol (0.38 g.) were dissolved in the smallest quantity of alcohol, a few drops of 10% alcoholic potash added and the mixture allowed to stand for 10-12 hours. The separated crystalline precipitate on examination was found to be a mixture of orange-yellow needles and white prismatic plates. The crystals were filtered and extracted with boiling acetic acid when the major portion of the orange-yellow substance together with very little of the white substance went into solution. The pre-

precipitate left after extraction with acetic acid was dissolved in chloroform and either ether or petroleum ether added to the chloroform solution when only the white prismatic plates separated.

This was filtered, m.p. 289-90°. The substance does not contain nitrogen. It is soluble in pyridine, almost insoluble in alcohol. It gives a straw-yellow colour with concentrated sulphuric acid and develops a greenish fluorescence after keeping for some time. (Found: C, 85.57; H, 4.42. $C_{12}H_8O$ requires C, 85.72; H, 4.76 per cent.).

The acetic acid extract was diluted with water and the separated precipitate after repeated crystallisations from acetic acid was identified to be bisacenaphthylidenediketone.

Condensations with *p*-nitrosodimethylaniline and nitrosothymol were next tried using alcoholic potash as the condensing agent, but the results were identical with that of the preceding experiment, only with this difference that the relative yields of the two products, viz., (1) bisacenaphthylidenediketone and (2) the white prismatic plates were somewhat different.

The experiments were also repeated by using diethylamine and piperidine respectively, as condensing agents, but with no better results and only the same two products could be isolated.

That the orange-yellow needles obtained in each attempt to condense acenaphthenone with nitroso compounds were identical with bisacenaphthylidenediketone (*vide infra*), was established in each case by mixed melting point determinations.

Condensation of Acenaphthenone with o-Diketones.

Bisacenaphthylidenediketone was easily obtained as orange-yellow needles by heating on the water-bath a solution of acenaphthenone (0.5 g.) and acenaphthenequinone (0.54 g.) in 10 c.c. of acetic acid with fused sodium acetate (2.3 g.) for 3-4 hours. After recrystallisation from acetic acid it melted at 287-88° (Graebe and Jequier give the m.p. 295°). (Found: C, 86.82. H, 3.85. $C_{24}H_{12}O_2$ requires C, 86.76; H, 3.61 per cent.).

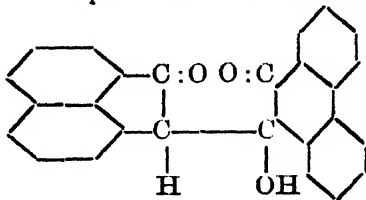
Aldol condensation of acenaphthenone and acenaphthenequinone.—The original filtrate from the preceding experiment was diluted with water, when a sticky solid separated. This was filtered and a portion of it was found to be highly soluble in alcohol, benzene, acetic acid or pyridine. The solid was extracted with cold alcohol and filtered from the insoluble residue. The filtrate was boiled with animal

charcoal and filtered. The filtrate on dilution yielded a microcrystalline powder which was then extracted with cold pyridine and filtered. To the hot pyridine solution hot water was slowly added when slightly pinkish plates separated on cooling. The crystals were filtered, washed repeatedly with dilute hydrochloric acid and then dried in a steam oven to free it from any pyridine left adhering, m.p. 168-69°. The yield of this product was very poor. The substance is slightly soluble in caustic potash solution with a blue fluorescence. In alcoholic potash it gives a green-coloured solution. It is highly soluble in alcohol, benzene, chloroform, etc. (Found: C, 82.73; H, 3.86. $C_{24}H_{14}O_3$ requires C, 82.28; H, 4.0 per cent.).

A better yield of the above aldol product (50 % after purification) was obtained by the condensation of acenaphthenone with acenaphthenequinone at a lower temperature (60-70°) and heating it for somewhat longer time (5-6 hours). Under these conditions the formation of bisacenaphthylidenediketone was entirely avoided.

The aldol product easily parted with water when heated for about $\frac{1}{2}$ - $\frac{3}{4}$ hour with excess of acetic anhydride and sodium acetate and yielded bisacenaphthylidenediketone, identified by mixed melting point determination.

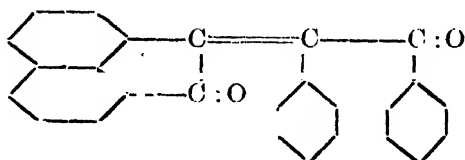
Condensation of Acenaphthenone with Phenanthraquinone.



Acenaphthenone (0.5 g.) and phenanthraquinone (0.62 g.) were dissolved in glacial acetic acid (15 c.c.) and sodium acetate (2.3 g.) added and was heated on the water-bath for 6-8 hours. No precipitate appeared during heating. After cooling the reaction mixture was diluted with water and the precipitate filtered. The solubility of the product thus formed was only very slightly different from that of phenanthraquinone whereas that of acenaphthenone was very different. By washing the precipitate with rectified spirit it was freed from acenaphthenone. The condensation product is less soluble in acetic acid than phenanthraquinone. Thus by repeatedly

dissolving the precipitate in acetic acid and then adding water in such a proportion as not to precipitate the whole thing, a product was obtained which however could not be crystallised from any solvent. It is fairly soluble in alcohol, highly so in benzene or chloroform. This product, purified from acetic acid by fractional precipitation by water, was obtained as a microcrystalline powder, decomposing at $185-87^{\circ}$, without melting. The yield, however, of the purified product was extremely poor. It dissolves in concentrated sulphuric acid with a greenish-yellow colour. (Found: C, 82.26; H, 4.64. $C_{26}H_{16}O_3$ requires C, 82.96; H, 4.25 per cent.).

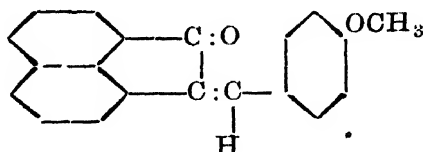
Condensation of Acenaphthenone with Benzil.



Acenaphthenone (0.5 g.) and benzil (0.63 g.) were dissolved in the smallest quantity of alcohol and a few drops of 10% alcoholic potash (10%) added, when immediately a beautiful crystalline precipitate separated. The filtered precipitate was washed with 50% alcohol and was purified by recrystallisation from dilute alcohol as glistening hexagonal yellow plates, m. p. 205° . It is sparingly soluble in absolute alcohol or acetic acid and highly soluble in benzene or chloroform. It dissolves in concentrated sulphuric acid with a scarlet red colour and is reprecipitated on dilution. (Found: C, 86.32; H, 4.42. $O_{26}H_{16}O_2$ requires C, 86.68; H, 4.4 per cent.).

Condensation of Aromatic Aldehydes with Acenaphthenone.

Anisylideneacenaphthenone.



Equimolecular quantities of acenaphthenone and anisic aldehyde were dissolved in the smallest quantity of alcohol and a few drops

of 10% alcoholic potash added. After some time a resinous product separated. This was filtered, washed with 40% alcohol, and then was dissolved in boiling alcohol, decolorised by animal charcoal and filtered hot. The filtrate, on dilution with a few drops of water, deposited on cooling beautiful yellow parallelepiped crystals, m. p. $126.5-27^{\circ}$. It is sparingly soluble in acetic acid or ether, highly soluble in chloroform or benzene. It gives a scarlet red solution with concentrated sulphuric acid and is reprecipitated on dilution. (Found: C, 83.51; H, 5.0. $C_{20}H_{14}O_2$ requires C, 83.90; H, 4.89 per cent.).

The following benzylideneacenaphthenones were prepared in a similar way (except where otherwise mentioned) as the preceding compound. They generally separated as solids without any difficulty.

m-Nitrobenzylideneacenaphthenone from acenaphthene and *m*-nitrobenzaldehyde separated from dilute alcohol in straw coloured rectangular plates, mixed up with some microcrystalline mass, m. p. $177-78^{\circ}$. It is highly soluble in benzene or chloroform and sparingly soluble in ether. It gives a blood-red solution with concentrated sulphuric acid and on dilution the original substance is reprecipitated. (Found: N, 4.87. $C_{19}H_{11}O_3N$ requires N, 4.65 per cent.).

p-Nitrobenzylideneacenaphthenone from acenaphthene and *p*-nitrobenzaldehyde, forms yellow silky needles from acetic acid, m. p. $239-40^{\circ}$. It is soluble in alcohol, acetic acid, and highly so in chloroform or benzene and is insoluble in ether. It gives deep red colour with concentrated sulphuric acid. (Found: N, 4.93. $C_{19}H_{11}O_3N$ requires N, 4.65 per cent.).

Cinnamylideneacenaphthenone from cinnamic aldehyde and acenaphthene, separated as a microcrystalline powder on the addition of water to the alcoholic solution of the reaction mixture after 24 hours of standing. It was purified by repeatedly dissolving in alcohol and reprecipitating by the addition of water containing a few drops of hydrochloric acid, m. p. $214-15^{\circ}$ with previous shrinking at 196° . It is soluble in benzene, chloroform or acetic acid. It gives an yellowish brown solution with concentrated sulphuric acid and is reprecipitated on dilution. (Found: C, 89.17; H, 5.1. $C_{21}H_{14}O$ requires C, 89.37; H, 4.96 per cent.).

Salicylideneacenaphthenone from salicylic aldehyde and acenaphthene, has already been described under pyrylium compounds.

(*J. Indian Chem. Soc.*, 1932, 9, 105), m. p. 186-87°. (Found: C, 83.79; H, 4.53. $C_{19}H_{12}O_2$ requires C, 83.81; H, 4.41 per cent.).

m-Hydroxybenzylideneacenaphthenone was prepared from *m*-hydroxybenzaldehyde and acenaphthenone in the same way as the preceding compounds and crystallised from dilute alcohol as pale yellow rectangular plates, m. p. 191-92°. It dissolves in alkali and in concentrated sulphuric acid with a reddish yellow colour. (Found: C, 83.51; H, 4.59. $C_{19}H_{12}O_2$ requires C, 83.81; H, 4.41 per cent.).

p-Acetylaminobenzylideneacenaphthenone, from acenaphthenone and *p*-acetylaminobenzaldehyde, crystallised from hot boiling alcohol in long yellow needles, m. p. 255.5-56°. It is soluble in chloroform or benzene. It dissolves in concentrated sulphuric acid with a reddish orange colour and is reprecipitated on dilution. (Found: N, 4.67. $C_{21}H_{15}O_2N$ requires N, 4.47 per cent.).

Preparation of isonitrosoacenaphthenone.—A mixture of acenaphthenone (1 g.) and amyl nitrite (1.03 g.) in alcohol (20 c.c.) was heated on the water-bath in a round-bottomed flask under a reflux. When the solution was just boiling hydrochloric acid (4.12 g., *d* 1.19) was added drop by drop. The colour of the solution changed from yellow to orange-red. Addition of hydrochloric acid was completed in about $\frac{1}{2}$ hour. On cooling a solid separated. To the cold mixture water was added and the precipitate filtered. This was extracted with dilute sodium hydroxide solution, when a part went into solution forming a reddish solution. The solution was then filtered and to the filtrate dilute acetic acid was added which gave a precipitate. This was crystallised from dilute alcohol in fine ash-coloured needles. The isonitroso compound thus prepared was found, as expected by theory, to be identical with the monoxime of acenaphthenequinone. This was confirmed by a mixed melting point determination.

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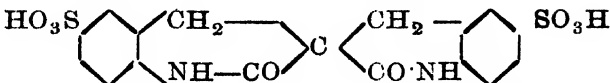
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